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CHARACTERIZATION OF LIQUID FUELS FROM SPOUTED BED PYROLYSIS OF CANADIAN COALS

Annual Report

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by

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TABLE OF CONTENTS

	Page
List of Figures	(i)
List of Tables	(ii)
Abstract	(iii)
1. Introduction	1
2. Apparatus	1
a. Low feed rate miniature screw feeder	1-6
b. The spouted bed pyrolyzer	6-10
c. Cyclone	10
d. The cryogenic traps	10
e. The solvent impingers	10-12
f. Temperature measurements	12
3. Experimental Procedure	13
a. Pyrolysis runs	13-15
b. Solvent fractionation of tar	15-16
c. Gas analysis	16
d. Char analysis	16
4. Pyrolysis Results - Effect of Variables	16-20
a. Coal feed rate	21
b. Effect of coal particle size	21
c. Effect of pyrolysis temperature	21-24
d. Coal agglomeration	24-29
5. Development of the Separation Scheme for Characterization of Hydrocarbons in Coal Tars	30-32
a. Prefractionation	33
b. Hydrocarbon group-type analysis by combined HPLC and capillary HRGC	33-36
6. Comparison of the Hexane Soluble Fractions (Oils) from the Miniature and Bench Scale Pyrolyzers	36-37
a. Procedure	37-39
b. Results and Discussion	39-44
7. Conclusions and Future Work	47
References	48
Appendix A: Personnel; paper and conference; project budget and committed expenditures, 1982-83	49
Appendix B: Proposed major tasks of characterization of liquids fuels from spouted bed pyrolysis of Canadian coals	50-52

LIST OF FIGURES

1. Coal Feeder (version 1)

2. Coal Feeder (version 2)

3. Teflon Rotor and Entrainment Nozzle Tube

4. Spouted Bed Pyrolyzer

5. Schematic Diagram of A Spouted Bed

6. All-Glass Micro-Cyclone

7. Spouted Bed Pyrolysis Unit

8. Calibration of Coal Feeder

9. Effect of Feed Rate on Tar Yield

10. Effect of Feed Rate on Gas Composition

11. Effect of Temperature on Product Yield (Feed Rate 12.8 ± .6 g/hr.)

12. Effect of Temperature on Hydrocarbon Gas Yield (Feed Rate 12.8 ± .6 g/hr.)

13. Effect of Temperature on Gas Yield (Feed Rate 12.8 ± 0.6 g/hr.)

14. Effect of Temperature on Hydrocarbon Gas Yield (Feed Rate 4.92 g/hr.)

15. Effect of Temperature on Gas Yield (Feed Rate 4.92 g/hr.)

16. Fractionation - Characterization Scheme for Coal Derived Liquids (Revised)

17. Separation and Characterization Scheme of Coal Tar

18. Dual Column HPLC Technique

19. HPLC of Combined Aliphatic and Aromatic Fraction Separated by CN-Bonded Phase Flash Chromatography

20. HRGC chromatograms of Aliphatic Sub-fractions from Run #59, 61, 62 and 64 (Bench Unit)

21. Chromatograms of Isolated Aliphatic Hydrocarbon Fraction

22. Total Ion Output of Hexane Eluted CN-Bonded Phase Flash Chromatographic Fraction of Coal Tar from Sukunka Coal (Run #8 at 500°C).

23. Selective Mass Ion Scanning

LIST OF TABLES

1. Analysis of Sukunka Coal

2. Solvent Fractionation of Sukunka Coal Tars

3. Pyrolysis Runs #6 to 15 for Sukunka Coal

4. Gas Yield, wt% of Coal Feed, as Received

5. Separation Scheme I - Solubility Classification
   Separation Scheme II - Volatility Classification

6. Tentative Assignment of Aliphatic Hydrocarbon Fraction from the Pyrolysis of Sukunka Coal on a Bench Scale Unit

ABSTRACT

This report describes work conducted in Fiscal Year 1982-83. A miniature, 2.5 cm. dia. spouted bed reactor with a continuous feed rate of 2.5-30 g/hr was developed to study the rapid pyrolysis of Canadian coal. A series of modifications from the original design were made to accommodate caking and non-caking coals of various sizes. The pyrolysis of Sukunka coal from the Peace River coal field was investigated with a vapor residence time of 0.4 second over a temperature range of 500-759^{o}C. Pyrolysis of this highly caking coal is essentially trouble-free. Conditions for maximum liquid yield have been established in terms of coal particle size, pyrolysis temperature and feed rate. Results are presented for liquid yield, gas yield and char yield. The gas yield is quantified in terms of species.

A method for classification of coal tars into major solvent-derived fractions was developed. The unique feature of the method allows for the further separation of the n-hexane soluble fractions "oils" into major compound classes by high performance liquid chromatography. Aliphatic alkanes (to C_{30}), alkylbenzenes (to C_4 - substituted) and alkylnaphthalenes (to C_4 - substituted) were found to be the major compound classes present in "oils" from Sukunka coal. Coal liquids (tars) produced in this work and by a larger 15 cm. dia. bench scale unit were investigated in detail by using the developed procedure concurrently with the high resolution gas chromatography - mass spectrometry study. The detailed composition of the aliphatic alkane sub-fraction is reasonably similar for all the tar samples generated from the bench scale pyrolyser and from this work. Extension of the work in terms of analyses of liquid fractions, and coal feedstocks is underway in the second year of work.

1. Introduction

The objectives of this work are to assess the quality of liquids produced by spouted bed pyrolysis of Canadian coals by separating pyrolysis liquids into fractions and characterizing these liquids in some detail (Appendix A). In the first year of the experimental investigation, which began on August 16, 1982 a micro-scale coal feeder, miniature spouted bed pyrolyser and trapping unit were designed, constructed and modified to give the required performance in terms of coal type, coal particle size, feed rate and pyrolysis temperature. Runs were completed for the highly caking Sukunka coal, a bituminous coal, under a nitrogen atmosphere. Analytical methods were developed concurrently with the equipment modifications and pyrolysis experiments.

The concept of short vapor residence time rapid pyrolysis or hydropyrolysis has been investigated by several research groups in Canada (1-4) as a means of achieving reasonable liquid yields from Canadian coals usually at temperature range of 500-850^{o}C and vapor residence time less than 1-2 seconds. While these coal liquids are readily obtainable in principle, the pyrolysis process suffers the disadvantage of low liquid yields. As well there is a lack of detailed information on liquid compositions. These features of rapid pyrolysis have been recently illustrated in Jarallah and Watkinson's work on pyrolysis of Western Canadian coals in a spouted bed (1).

Among the advantages of the spouted bed pyrolyzer is its ability to handle a wide range of coal particle sizes from fraction of a millimeter to several millimeters and its ability to overcome the agglomeration of caking coal in the pyrolysis process. Some attention has to be paid to reactor configuration to achieve these advantages.

2. Apparatus

(a) Low Feed Rate Miniature Screw Feeder

The continuous micro-pyrolyzer required a feeder capable of providing a

constant coal feed rate of the order of about 20-100 g/hr.

(i) Version 1: The feeder shown in Figure 1a was the original design capable of handling coal particles of size range 350 to 25 μm for feed rate 2.5 to ca. 30 g/hr. Two different configurations of the screw feeder were tested for coal particles of different physical characteristics. For feed rates as low as 2.5 g/hr. for finer coal -75 + 0 μm, the preferred configuration is shown in Figure 1a. Figure 1b shows the preferred configuration for coal samples with higher moisture content and/or of coarser particle size. The Teflon rotor (Figure 1c) was used in place of the pivot to control and clear the feeding through the 5mm opening. The lower channel to the left of Figure 1b was closed and the nozzle tube was shifted to the upper channel immediately below the inverted V-shaped chamber. Constant feed rates as high as 60-90 g/h have been achieved. For both configurations, a slightly positive nitrogen pressure was maintained inside the coal hopper, using a nitrogen flow rate of 1.2-1.8 l/min. Calibration of feed rate was carried out for individual coal samples of a given size range prior to the pyrolysis run. An identical spouted bed unit constructed from plexiglass was substituted for the stainless steel pyrolysis unit. 20 g of Ottawa sand (-430 + 425 μm) was introduced into the plexiglass unit and a cotton plug was used to retain all coal particles spouting over a given period of time. From the weight gained, the feed rate was calculated.

The main disadvantage of this feeder are the time consumed in adjusting the feed rate to the desirable range and in carrying out the calibration.

(ii) Version 2: The feeder shown in Figure 2 was the modified and reconstructed design capable of handling coal particles of size range 450 to 25 μm for a feed rate 2.5 to 30 g/h.

The feed hopper is a cylinder with a screw top to facilitate loading. The Teflon rotor shaft enters through the screw top via the Teflon ferrule. The screw drill at the end of the rotor shaft fits exactly into the inserted stainless

FIGURE 1

COAL FEEDER (version 1)

(a) (b) (c)

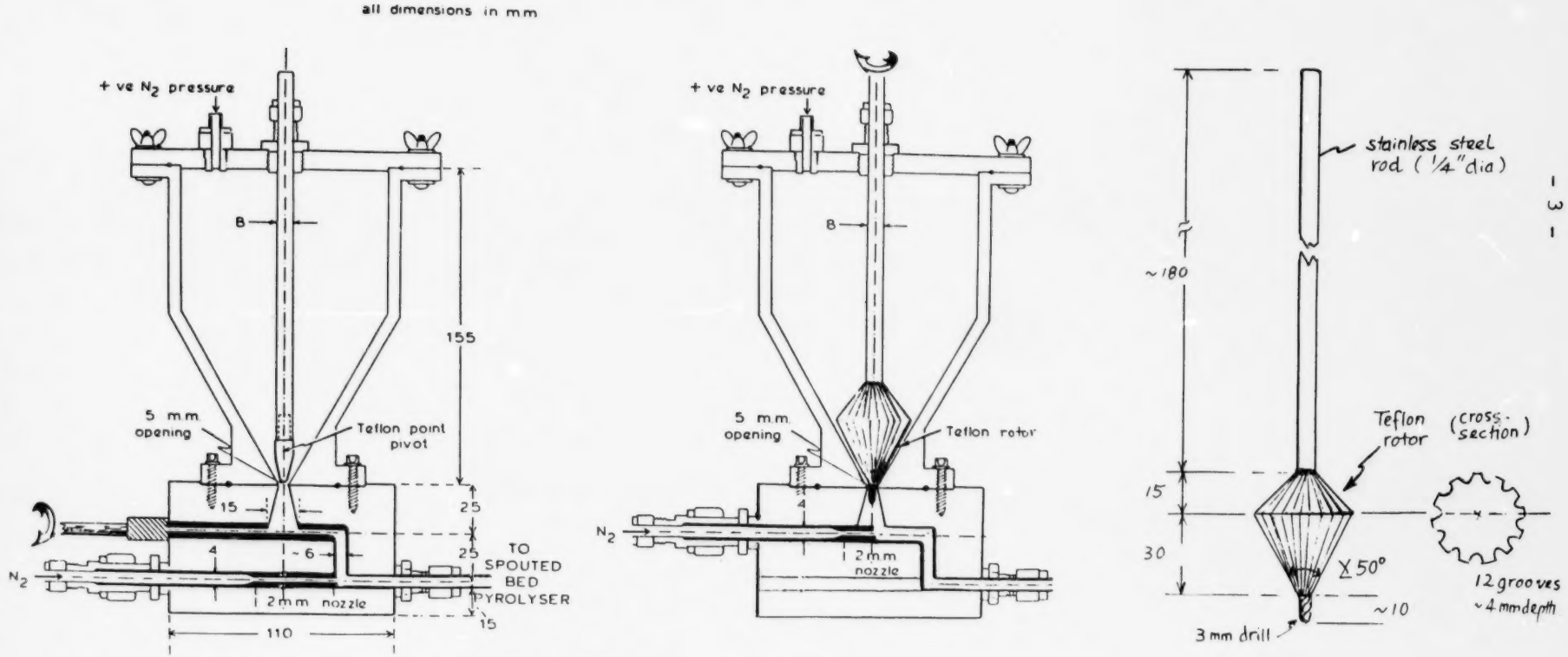


FIGURE 2

COAL FEEDER (version 2)

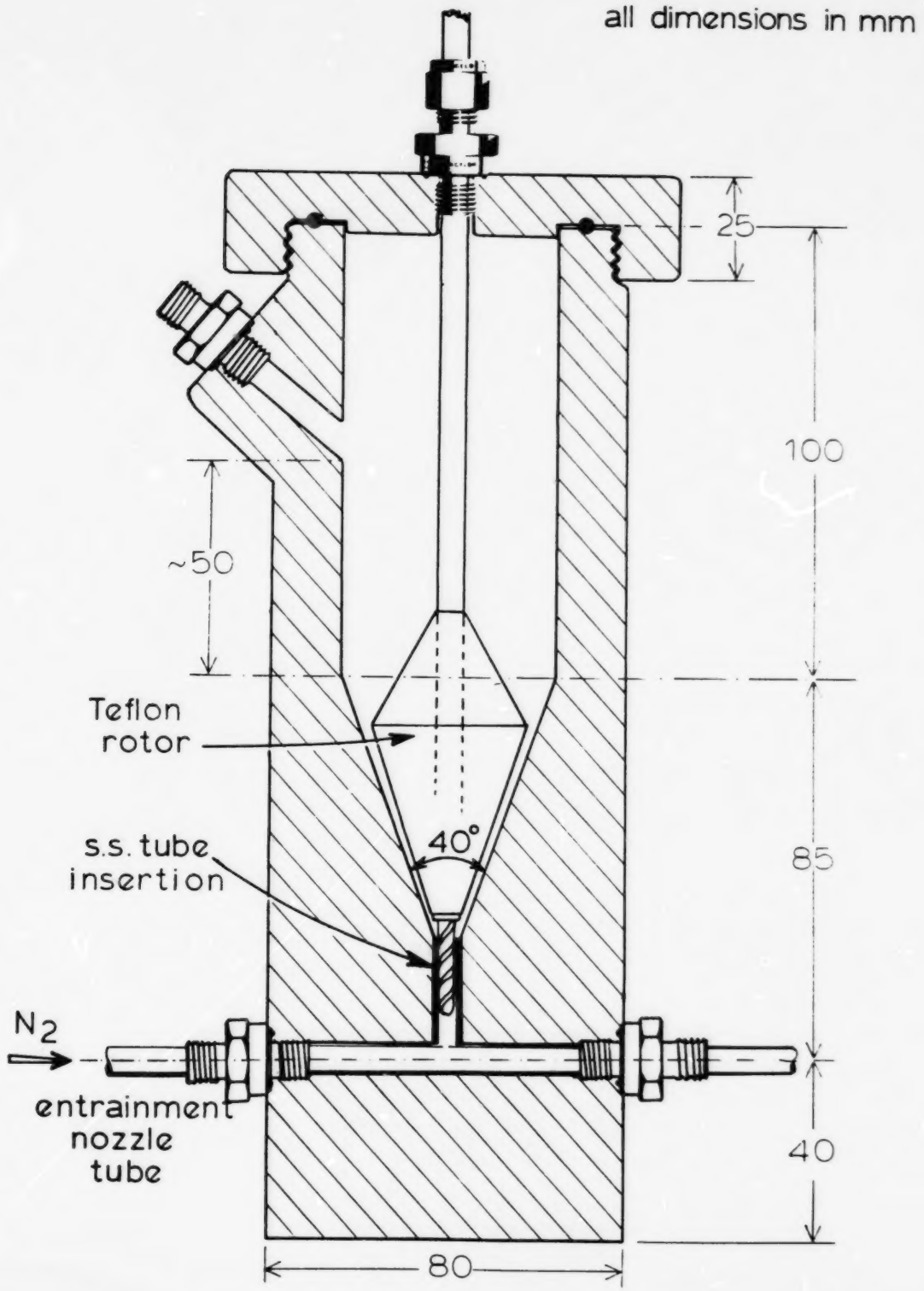
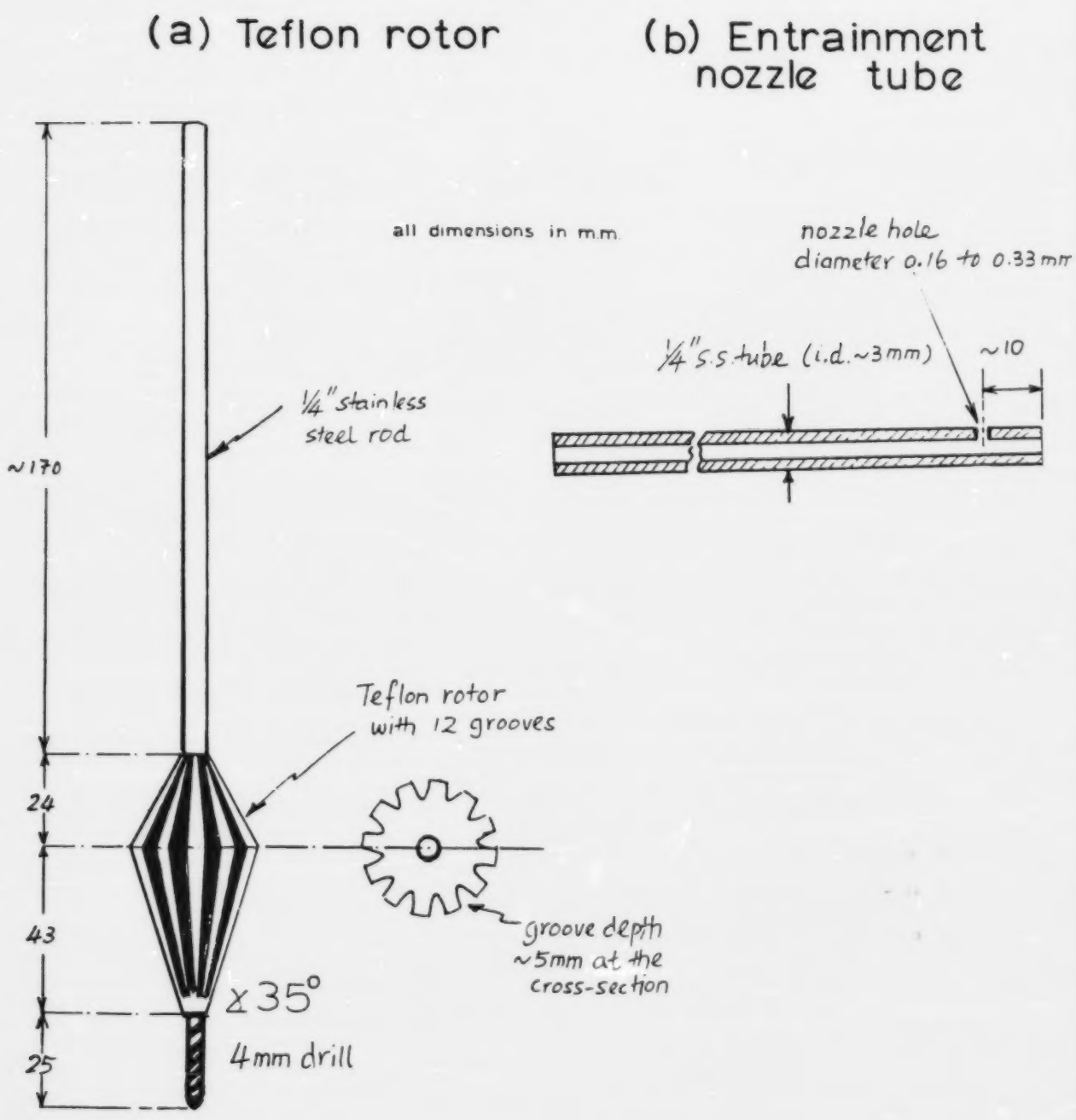


FIGURE 3


(a) Teflon rotor
(b) Entrainment nozzle tube
all dimensions in m.m.
nozzle hole diameter 0.16 to 0.33 mm
¼" S.S. tube (i.d. ~3mm)
~10
¼" stainless steel rod
~170
Teflon rotor with 12 grooves
24
43
25
groove depth ~5mm at the cross-section
∠35°
4mm drill

steel tube at the bottom of the feed hopper. The carrier gas entrainment nozzle tube (Figure 3b) is located just below the inserted stainless steel tube consists of a small orifice hole 0.16 to 0.33 cm according to coal type and feed rate desired. Gas was fed to the entrainment nozzle tube at a sufficient rate to transport the coal particles coming through the grooves of the Teflon rotor (Figure 3a) and the small orifice. The feed gas line had an equalizing connection to the freeboard of the hopper via the side arm on the hopper. In order for the entrained coal particles to spout through the silica sand bed (ca. 4.5 cm deep) a minimum gas feed rate is required. In practice, a gas feed rate of 1.5-3.5 l/min was used to yield a gas/coal weight ratio of about 15-55:1. For non-spouted bed applications the gas/coal weight ratio could have been lowered.

(b) The Spouted Bed Pyrolyzer

The pyrolyzer was constructed from 316 stainless steel (I.D. 25 mm x length 150 mm) with a cone angle of 70° at the bottom (Figure 4). An exchangeable inlet orifice tube of 40 mm in length was provided with internal opening diameters of 2 and 3.3 mm.

The furnace for the pyrolyzer was built from two Lindberg semi-cylindrical heating elements with I.D. = 1½ inches. The electrical output is 660 watts and provides temperatures as high as $950^{\circ}C$. The heating elements are encased in a steel shell lined with refractory.

The spouting behaviour of different size ranges of Ottawa silica sand (430 to 250 μm) was studied in an identical spouted bed system constructed from plexiglass. Figure 5 shows a schematic diagram of a spouted bed in action. The minimum spouting velocity U_{ms} of silica sand by nitrogen gas at atmospheric pressure and room temperature ($25^{\circ}C$) can be approximated by the following expression, determined empirically from our test results:

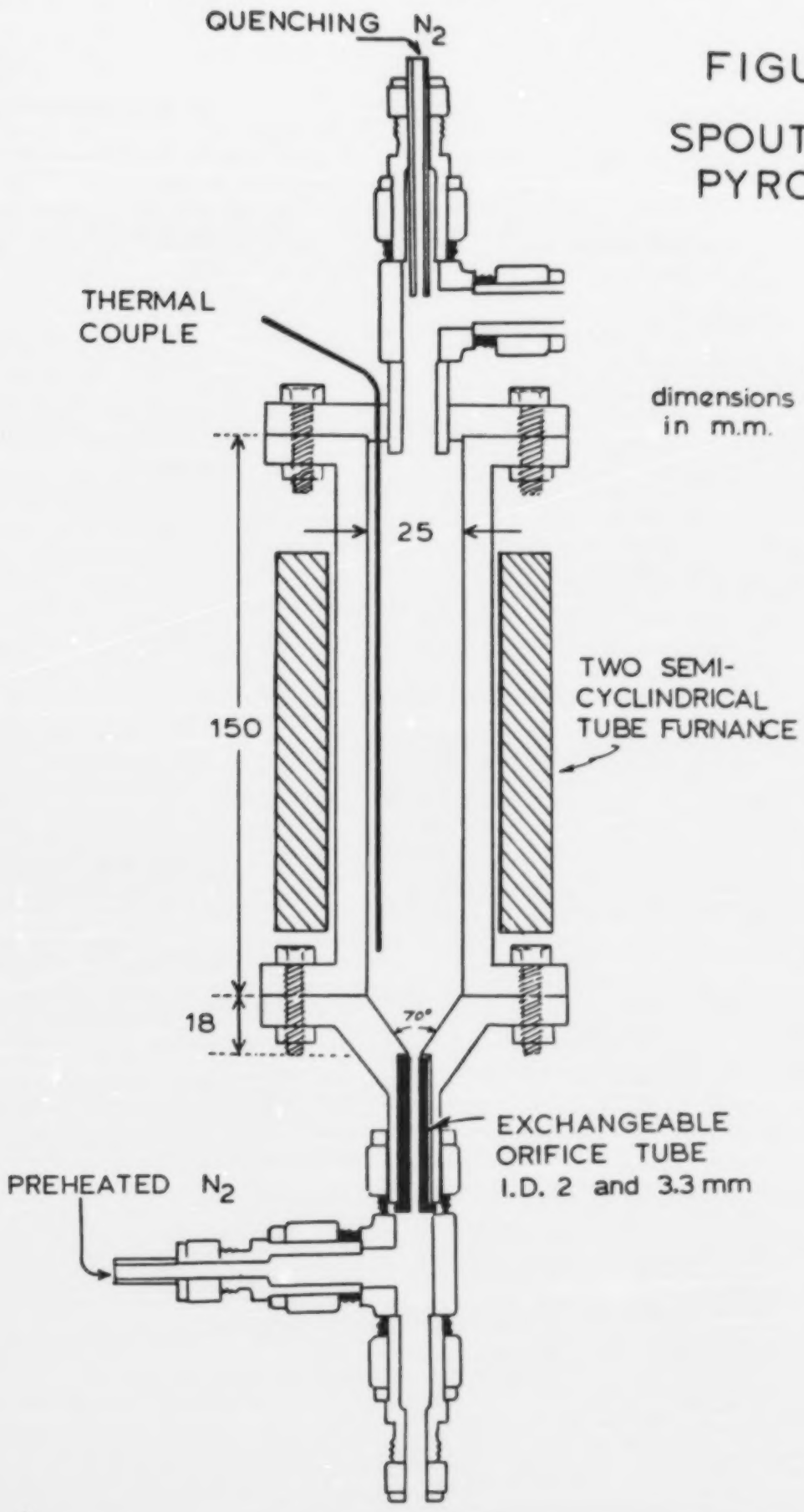
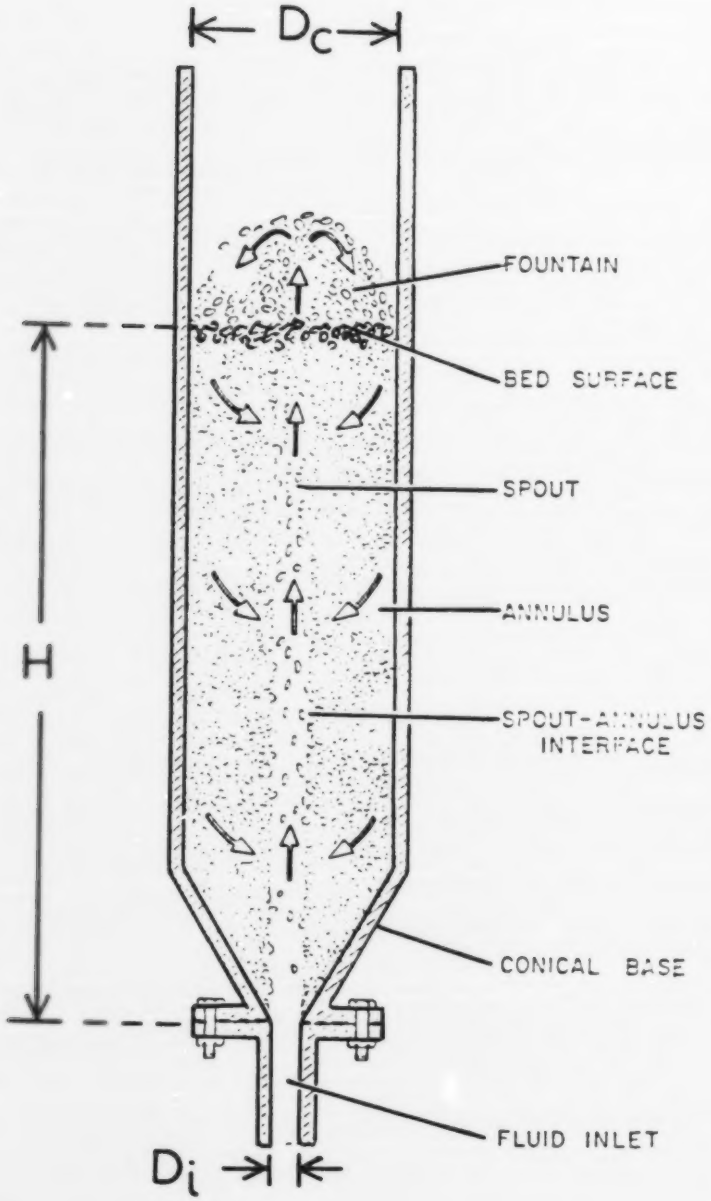


FIGURE 4

SPOUTED BED PYROLYSER

FIGURE 5

SCHEMATIC DIAGRAM OF A SPOUTED BED



$$U_{ms} \simeq 310\ \bar{d}_p\ \sqrt{H}\ (D_i)^{1/3},\ \text{cm-sec}^{-1} \qquad (1)$$

where $\bar{d}_p$ = average particle diameter of sand (cm)

H = bed depth (cm)

D_i = N_2 gas inlet diameter (cm)

The generalized Mathur-Gichler equation for a macro spouting system is expressed as:

$$U_{ms} = \frac{\bar{d}_p}{D_c}\left(\frac{D_i}{D_c}\right)^{1/3}\sqrt{\frac{2gH(\rho_s-\rho_f)}{\rho_f}} \qquad (2)$$

where D_c = column diameter

g = acceleration of gravity

ρ_f = fluid density

ρ_s = particle density

In this study D_c = 2.5 cm, ρ_s = 2.64 g-cm^{-3} (SiO_2) ρ_f = 1.152 x 10^{-3} g-cm^{-3} (N_2 at 25^{o}C), g = 980 cm-sec^{-2}.

The U_{ms} can be derived from equation (2) and expressed as

$$U_{ms} = 625\ \bar{d}_p\ \sqrt{H}\ (D_i)^{1/3},\ \text{cm-sec}^{-1} \qquad (3)$$

It was noted that the pre-coefficient of equation (3) is roughly double that of equation (1).

For the micro spouted bed system in this study, equation (1) was used in predicting the minimum N_2 flow rate (cm^3 - sec^{-1}) required to spout the silica sand bed composed of average particle size $\bar{d}_p$ for a defined bed depth H, with a given N_2 inlet nozzle diameter D_i. Conversion of this minimum N_2 flow rate at 25^{o}C to the desired working temperature was then done using the ideal gas law.

In practice, in pyrolysis runs conducted at 500^{o}C for spouted bed height H = 4.5 cm with average particle diameter of $\bar{d}_p$ = 0.0427 cm, it was found that a nitrogen flow rate of 60 cm^3/sec (at 25^{o}C) would provide a stable spouted bed for coal pyrolysis. The minimum nitrogen flow rate as calculated from equation (1)

for operating such a spouted bed at 500°C using 2.2 mm inlet nozzle shown to be 52 cm^3/sec which is ca. 15% less than the actual operating flow rate.

This miniature spouted-bed pyrolyzer was able to handle relatively large coal particle sizes up to 425 μm for non-caking coal and up to 250 μm for highly caking coal. For details on the mechanism of spouted beds, the reader is referred to the book by Mathur and Epstein (5).

(c) Cyclone

A cyclone, located downstream of the nitrogen quencher was used to separate the char particles from the gas and hot vapor. A miniature cyclone originally constructed from stainless steel was later replaced by a pyrex glass cyclone (Figure 6). The char receiver has a capacity of 50 cm^3. The inlet to the cyclone was connected to the pyrolysis reactor via a metal to glass adapter. This design was adopted for ease and quantitative removal of char and possible adhering tar deposits. It was observed that char collected in the receiver flask was relatively clean and sufficiently free from tar contamination to be free-flowing.

(d) The cryogenic traps

The trapping train (Figure 7) consisted of three cryogenic traps for maximum tar condensation. Each trap was packed with ca. 5 cm of ceramic packing pieces to increase the condensation of tar and improve tar droplet collection. Glass-wool was originally used for this purpose, but it often blocked due to solidification of tar condensate a liquid nitrogen temperature (-197°C) causing a pressure rise and necessitating a shut down of the system.

(e) The solvent impingers

The two solvent impingers were located downstream of the cryogenic train (Figure 7). The impinger tubes had a fritted glass end. Methylene chloride and hexane were used in the first and second impingers respectively. These were both immersed in an ice-bath during the pyrolysis runs.

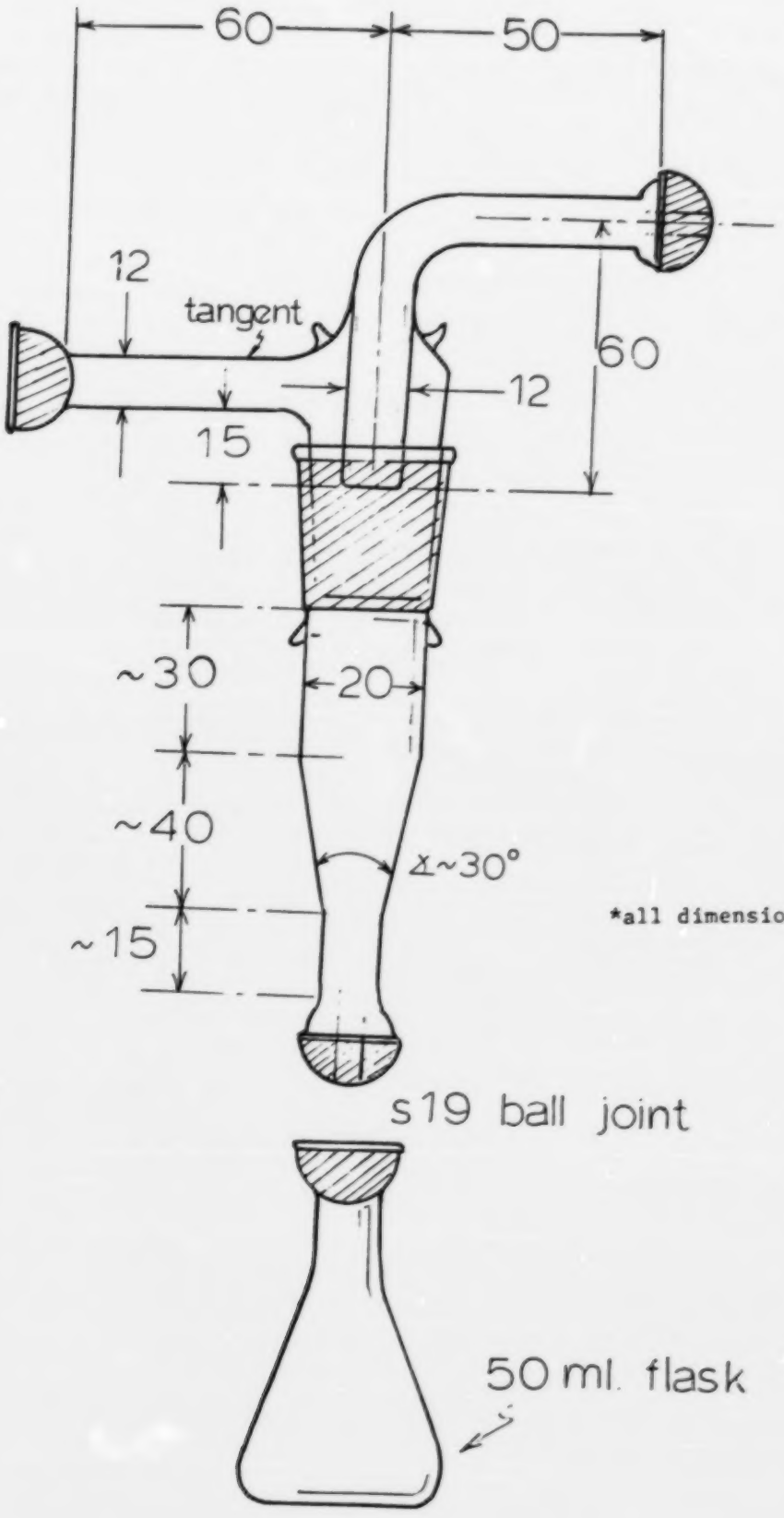


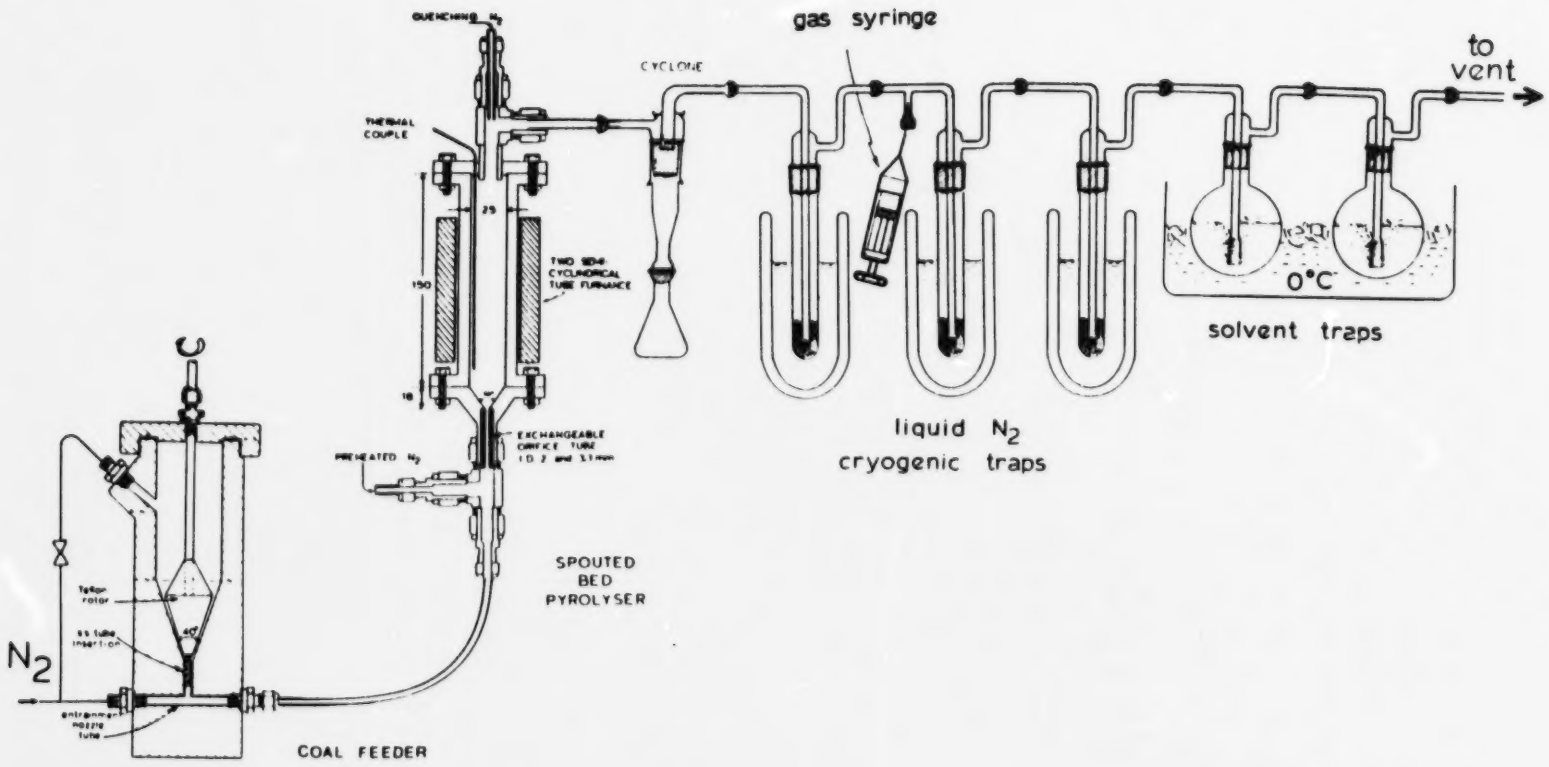
FIGURE 6

ALL-GLASS MICRO-CYCLONE

*all dimensions in mm

FIGURE 7

SPOUTED BED PYROLYSIS UNIT



(f) Temperature measurements

The temperature throughout the whole pyrolysis unit was measured by chromel-alumel thermocouples (1.6 mm x 30 cm length) with 316 stainless steel sheaths. Thermocouples were located in the spouted bed (ca. 2 cm from the sand surface), at the port of coal injection, the feed gas preheater, the preheated feed gas outlet and the port of N_2 quenching prior to the cyclone inlet.

3. Experimental Procedure

(a) Pyrolysis Runs

The unit shown in Figure 7 was operated under the following conditions.

Coal size range = -250 + 125, -125 + 75, -75 + 0 μm

Coal feed rate = 2.8 - 20 g/hr

Temperature = 500 - 750°C

Spouted bed material = Ottawa sand (-430 + 425 μm)
20 - 25 g

Nitrogen feed rate = 3.5 - 5.5 l/min.

Run time = 30 - 60 minutes

Vapor residence time in spouted bed ≈ 0.1 sec.

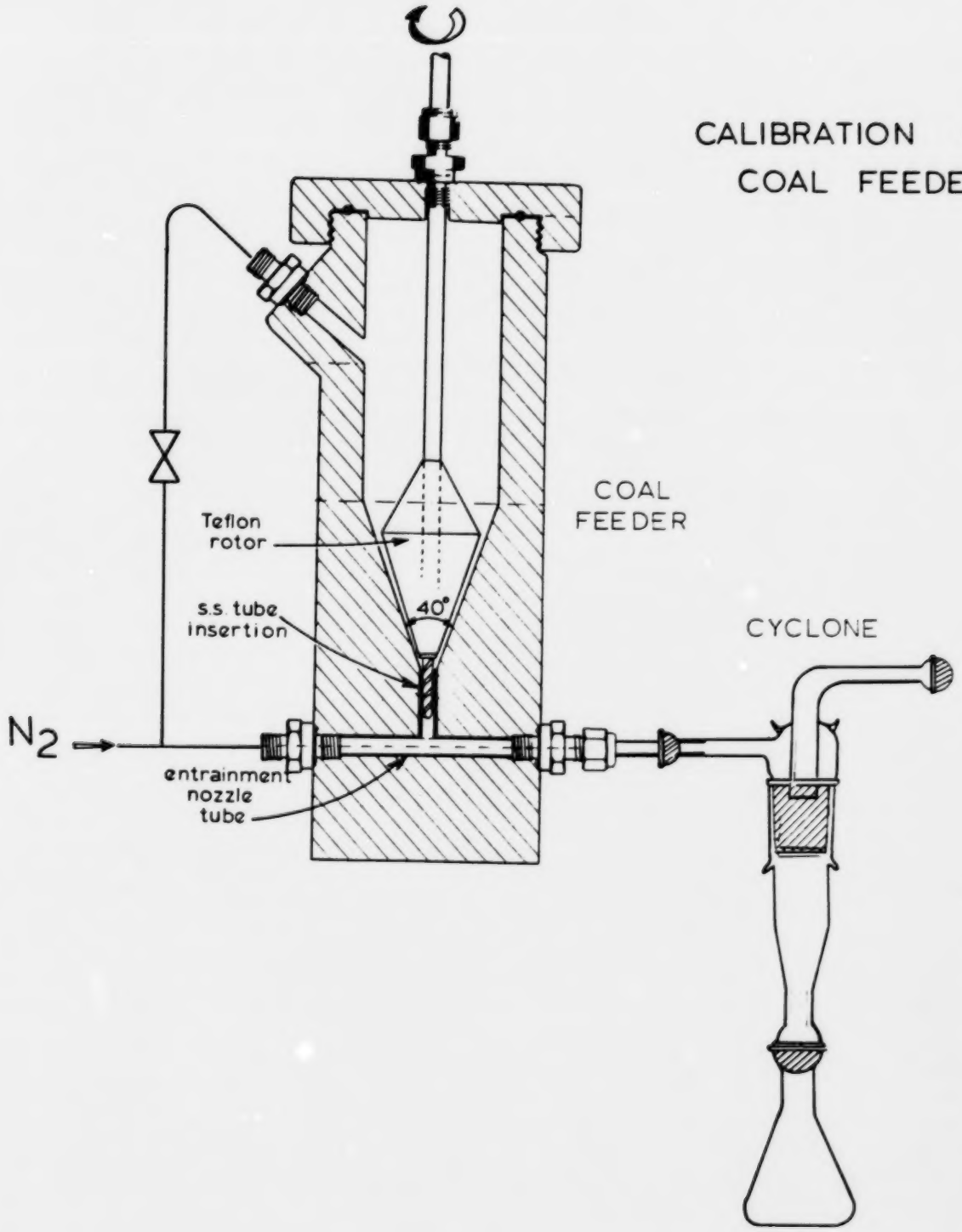
Vapor residence time in pyrolyzer ≤ 0.43 sec.

The procedure for a run was as follows:

The weighed feeder containing the coal was first calibrated using the all-glass-cyclone unit over a period of time (5-10 min) under a fixed entrainment gas flow, a constant rotor speed (6-25 rpm) and a given orifice size (Figure 2b). The calibration set-up was shown in Figure 8.

The coal injection tube from the feeder met the preheated entrainment gas (250-350°C) via the stainless steel tee just below the nozzle tube. The stainless steel reactor was filled with accurately weighed sample of Ottawa sand (20-25 g). A low flow of entrainment gas was sent through the sand bed during heating, with the orifice hole of the feeder closed (i.e. by turning the orifice tube 180°).

FIGURE 8


CALIBRATION OF
COAL FEEDER
COAL
FEEDER
Teflon
rotor
s.s. tube
insertion
40°
CYCLONE
N2
entrainment
nozzle
tube

The all-glass-cyclone, cryogenic trapping train and solvent absorption traps were prepared and put in place.

A run was begun by turning the orifice hole of the feeder to the upward position, with the rotor on and the entrainment gas flow at the set rate. A 1-cm^3 gas sample was taken every minute downstream of the first cryogenic trap (Figure 7) to fill a gas sampling syringe over a period of 10 minutes. A run was generally 30-60 minutes in length.

The coal feed rate was double checked from the weight lost over the period of coal feeding. Tar yield was obtained directly from the weight gain on the cryogenic traps. Char yield was derived from the weight gain on the cyclone, as no char remained in the bed in normal operation. The gas yield was calculated from the total entrainment gas flow through the unit and the gas composition analysed on a Varian GC equipped with a methanizer and flame ionization detector.

(b) Solvent Fractionation of Tar

HPLC grade n-hexane was used to extract for 5 minutes under ultrasonic conditions the soluble oil from the tar collected in the cryogenic traps. The hexane extract was then combined and filtered through a 0.45 μm micropore Teflon filter and the volume of filtrate was recorded. The filtrate was sealed and stored in freezer (-20°C) for further analysis. HPLC grade tetrahydrofuran (THF) was used to remove the remaining tar in the traps. It was found that all fresh tars were completely solubilized in THF. The THF filtrate was subjected to flash evaporation near dryness under reduced pressure (ca. 15 mm Hg) at 55°C on a rotary evaporator. 50 ml of spectroscopic grade benzene was added and extraction in an ultrasonic bath for ca. 5 minutes. The homogenized solution was filtered over a preweighed 0.45 μm micropore Teflon filter. The weight of the benzene insoluble - THF soluble fraction was taken. The benzene filtrate was again subjected to evaporation until dryness under the same conditions as

for THF filtrate and the weight of hexane insoluble-benzene soluble fraction was recorded.

(c) Gas Analysis

Gas samples were analyzed on a Varian Vista GC equipped with a flame ionization detector and a Ni-catalyst for methanizing CO and CO_2 to CH_4 at 350-380°C. A dual column method and a 6-port loop valve was used for complete resolution and quantification of CO_2, C_2H_4, C_2H_6, C_2H_2, CO and CH_4 gases. Unfortunately, helium was used as the GC carrier gas, the detection of hydrogen gas with a thermal conductivity detector upstream of the methanizer was poor for volume concentrations of 3% or less.

GC conditions: Porapak N (60/80 mesh, 1/8" x 12') and Molecular Sieve 13 x (60/80 mesh, 1/8" x 10'). He flow rate 20 ml/min., H_2 = 20 ml/min. under isothermal conditions (60°C). Supelco gas mix standard containing 1% (by volume) each of CH_4, C_2H_4, C_2H_6, C_2H_2 CO and CO_2 was used for the calibration.

(d) Char Analysis

The char analysis for C, H, N and S will be contracted out to a local commercial analysis service. Proximate analysis will be conducted on a Perkin-Elmer TGA-2 system on the thermogravimetric analysis mode to generate data on moisture, remaining volatile matter, fixed carbon and ash contents. Petrographic analysis will be performed by Brian Kyberg of the University of Regina.

4. Pyrolysis Results - Effect of Variables

Results of pyrolysis runs of Sukunka coal are presented in detail in Tables 3 and 4. Sukunka coal is a bituminous coal (Table 1) from the Peace River Coalfield of British Columbia. It was found that this highly caking coal with high free swelling index (FSI = 7) can be readily pyrolyzed in the micro spouted-bed pyrolyzer without creating agglomeration problems under appropriate conditions.

TABLE 1

Analysis of Sukunka Coal

Proximate Analysis		Ultimate Analysis(wt%,maf)
% moisture	1.08	C = 89.98
% volatiles	20.60	H = 4.53
% fixed carbon	65.14	S = 0.69
% ash	13.18	N = 1.75
		O (by diff) = 3.05
		H/C = 0.60

Maceral Analysis (volume %)	
Vitrinite	65.3
	27.7
Exinite	6.9

TABLE 2

Solvent Fractionation of Sukunka Coal Tars

Run #	Pyrolysis Temp, °C	Fraction		
		Hexane soluble	Benzene sol. hexane insol.	THF soluble benzene insol.
This work				
8	500	14.7	57.7	27.6
12	550	17.1	65.6	17.3
13	600	20.3	73.1	6.6
15	650	22.0	68.5	9.5
Jarallah's work(a)				
48	520	14	73	13
67	580	21	69	10

(a) From a larger bench unit

TABLE 3

Pyrolysis Runs #6 to 15 for Sukunka Coal

Run #	Coal particle size, μm	Feed rate g/hr	Temp. °C	Product Yield Gas	Tar	Char	(Closure)
6	-75 + 0	0.4	550		N.A.		-
7	-125 + 75	2.3	550		16		-
8	-125 + 75	5.4	500		17.0		-
9	-450 + 250	(a)	500		N.A.		-
10	-250 + 125	5.1(b)	500	4.9	8.2		-
11	-250 + 125	11.6	500	4.9	18.1	55.0	(78.0)
12	-250 + 125	12.2	550	16.9	16.7	66.2	(99.8)
13	-250 + 125	14.0	598	22.0	29.6	54.3	(105.4)
15	-250 + 125	13.8	648	17.9	28.3	45.0	(91.2)
Run # 14a to 14f (10 min. run per temperature point)							
14a	-250 + 125	4.9	454	3.8		N.A.	
14b	-250 + 125	4.9	500	5.6			
14c	-250 + 125	4.9	551	7.1			
14d	-250 + 125	4.9	598	10.3			
14e	-250 + 125	4.9	650	11.6			
14f	-250 + 125	4.9	698	21.4			

(a) Test failed due to char agglomeration in reactor

(b) 15 min. run due to frozen tar blockage in the first cryogenic trap.

TABLE 4

Gas yield, wt% of coal fed, as received

Run #	Temp °C	CO	CO_2	CH_4	C_2H_6	C_2H_4	C_2H_2
10	500	1.12	.486	1.91	.06	.29	$.00_3$
11	500	1.58	1.69	.70	.43	.50	.02
12	550	5.20	9.14	1.29	.34	.95	.05
13	598	6.68	12.27	1.64	.23	1.06	.07
15	648	10.03	4.17	2.15	.22	1.16	.17
14a	454	-	3.62	.15	-	-	-
14b	500	2.77	1.84	.74	.10	.16	-
14c	551	4.12	1.55	.99	.11	.27	.02
14d	598	6.53	1.41	1.41	.19	.69	.06
14e	650	7.90	1.17	1.55	.30	.57	.06
14f	698	15.50	2.80	2.00	.11	.86	.10

(a) Coal Feed Rate

The effect of coal feed rate on tar yield at 500 and 550°C for two different size ranges of coal is shown in Figure 9. The tar yield remains relatively constant for feed rates below about 15 g/hr. In the extreme case, where a high feed rate of 51 g/hr was used, char agglomerates were found to accumulate inside the reactor immediately above the bed and cause blockage. The tar yield may be expected to be lower for this situation due to the entranced secondary reactions, such as cracking and polymerization of tar vapor over the abundant hot char surface.

Gas analysis for the three different feed rates 4.9, 11.6 and 51 g/hr at 500°C (Figure 10) indicates that feed rate of the two extremes does not offer any advantages for a more constant gas composition with less dependence on the feed rate. From the current work on Sukunka coal, based on tar and gas yield as well as gas composition, the best working range for feed rate is 10-15 g/hr for this micro reactor. This working range is equivalent to 20-30 kg/hr m^2. Recent work of Jarallah and Watkinson (1) in a 15 cm diameter unit has shown that a maximum tar yield of 31% (maf basis) was obtainable for an average particle size of 3.4 mm at 580°C using a feed rate of 50 kg/hr m^2.

(b) Effect of Coal Particle Size

Figure 9 also demonstrates that tar yields for coal particles of size -250 + 125 μm and -125 + 75 μm were not significantly different. In this work a maximum tar yield of 35.2% (maf basis) has been achieved for coal particle -250 + 125 μm at 600°C (Figure 11) which compares favourably to the 31% (maf basis) obtained by Jarallah and Watkinson (1) on 3.4 mm coal particles and previously cited.

(c) Effect of Pyrolysis Temperature

Pyrolysis as a thermal cracking process for distingration of coal matrix into its simple constituent molecular moieties was well utilized in the past for

FIGURE 9

Effect of Feed Rate on Tar Yield

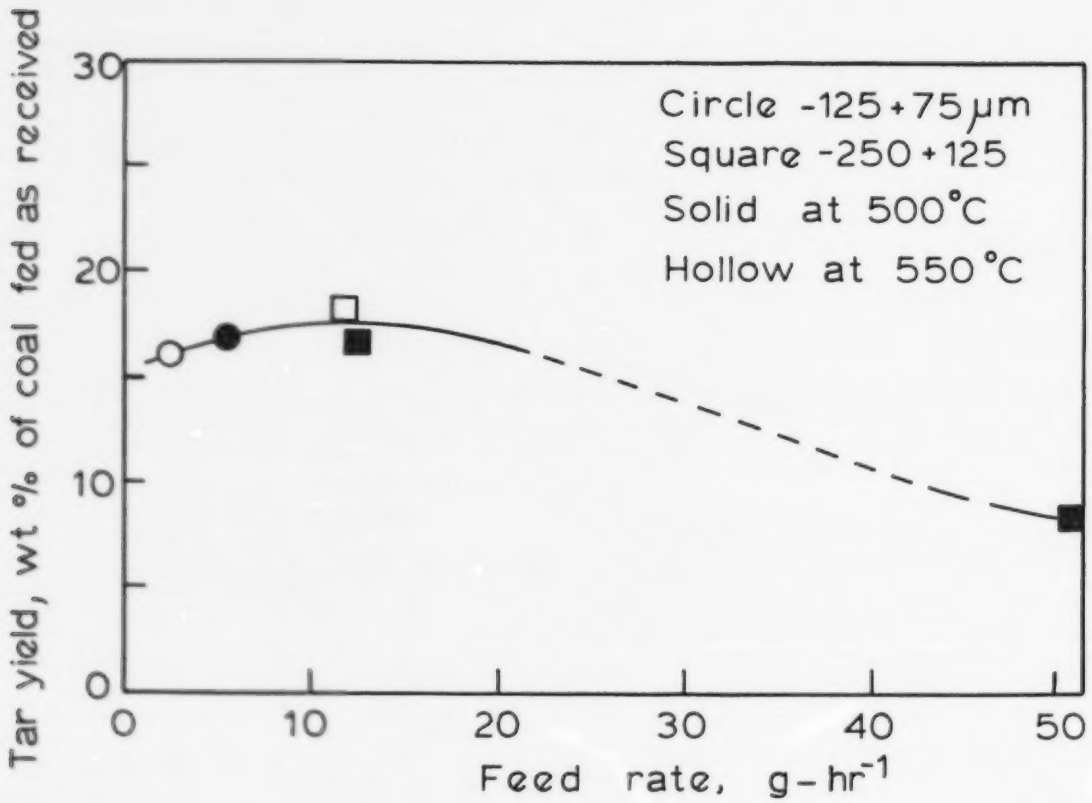
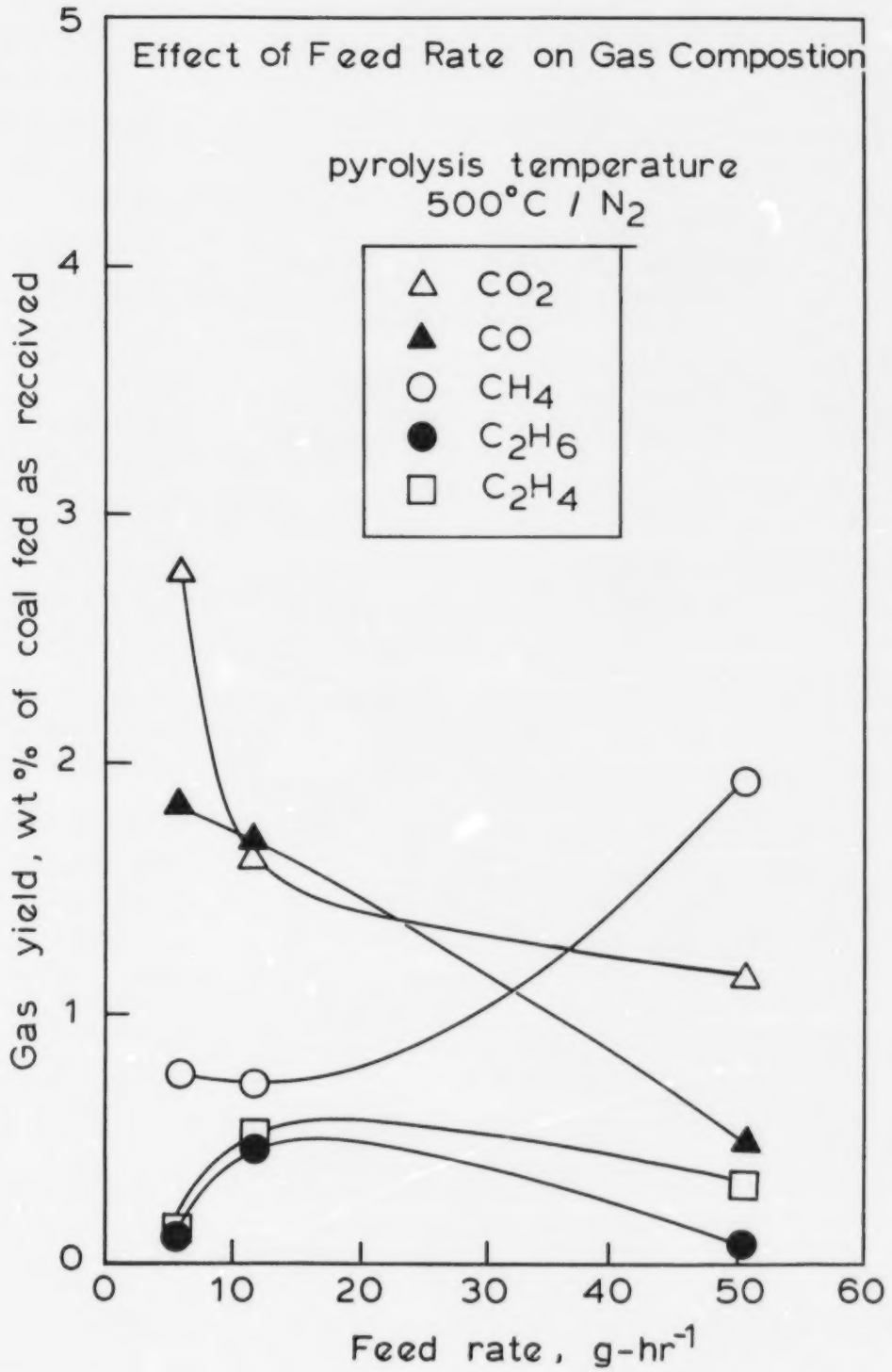


FIGURE 10


Effect of Feed Rate on Gas Compostion
pyrolysis temperature
500°C / N2
CO2
CO
CH4
C2H6
C2H4
Gas yield, wt% of coal fed as received
Feed rate, g-hr-1
0
1
2
3
4
5
0
10
20
30
40
50
60

deriving useful chemicals, particularly the aromatics, from coals. The tar yield and its quality both strongly rely on the nature of the coal used and the character of the thermal process itself (7,8). Undoubtedly, pyrolysis temperature is the prime factor in the pyrolysis process. In this study it was found that gas and tar yields both reached a maximum at the vicinity of 600°C (Figure 11). Gas analysis reflects that methane formation somehow varies rectilinearly over the temperature of 500-700°C (Figures 12 and 14). The presence of unsaturated hydrocarbons represented by ethylene (C_2H_4) and acetylene (C_2H_2) is shown to be favoured by higher temperature. This finding also implies that thermal cracking tends to be greater for the saturated hydrocarbon species at higher pyrolysis temperatures as represented by the general decline in ethane yield towards 700°C. The temperature effect on the overall gas composition using two different ranges of coal feed rate (Figures 12 to 15) shows the same trends for both light hydrocarbon gas yield ($CH_4 + C_2H_2 + C_2H_4 + C_2H_6$) and CO gas yield. The temperature profile of CO_2 production appear to be drastically different for the two different feed rates. The reason for this is unclear.

(d) Coal Agglomeration

In some of the preliminary test runs on Sukunka coal using high feed rate (e.g. 51 g/hr) for particle sizes of -250 + 125 μm and moderate feed rates (20-30 g/hr) for coarser coal particles -450 + 425 μm, the product chars were found retained within the freeboard space above the spouted bed. This suggests that although agglomeration within the bed is minimized due to high linear gas velocity through the spout-annulus interface (Figure 7) and the violent attrition, under certain conditions the heated coal particles swell and transform into a sticky mesophase, which mixes with some sand grains and adheres to the reactor exit ducting (Figure 4). There is obviously a range of conditions under which reactor operation is impossible with highly caking coals. For all the successful pyrolysis runs, no char particles were found to be retained in the sand bed and/or in the pyrolyzer.

FIGURE 11

Effect of Temperature on Product Yield

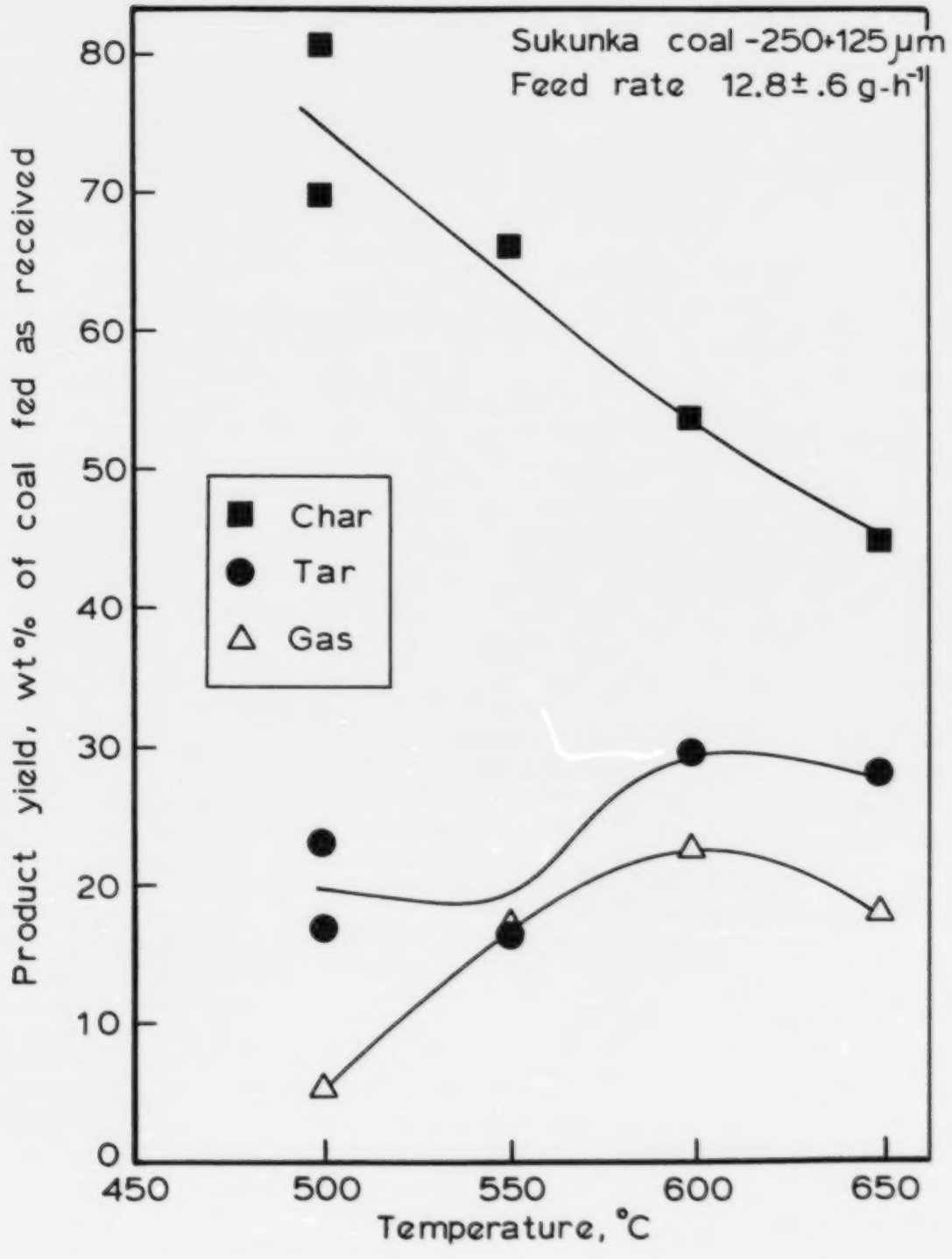


FIGURE 12

Effect of Temperature on Hydrocarbon Gas Yield

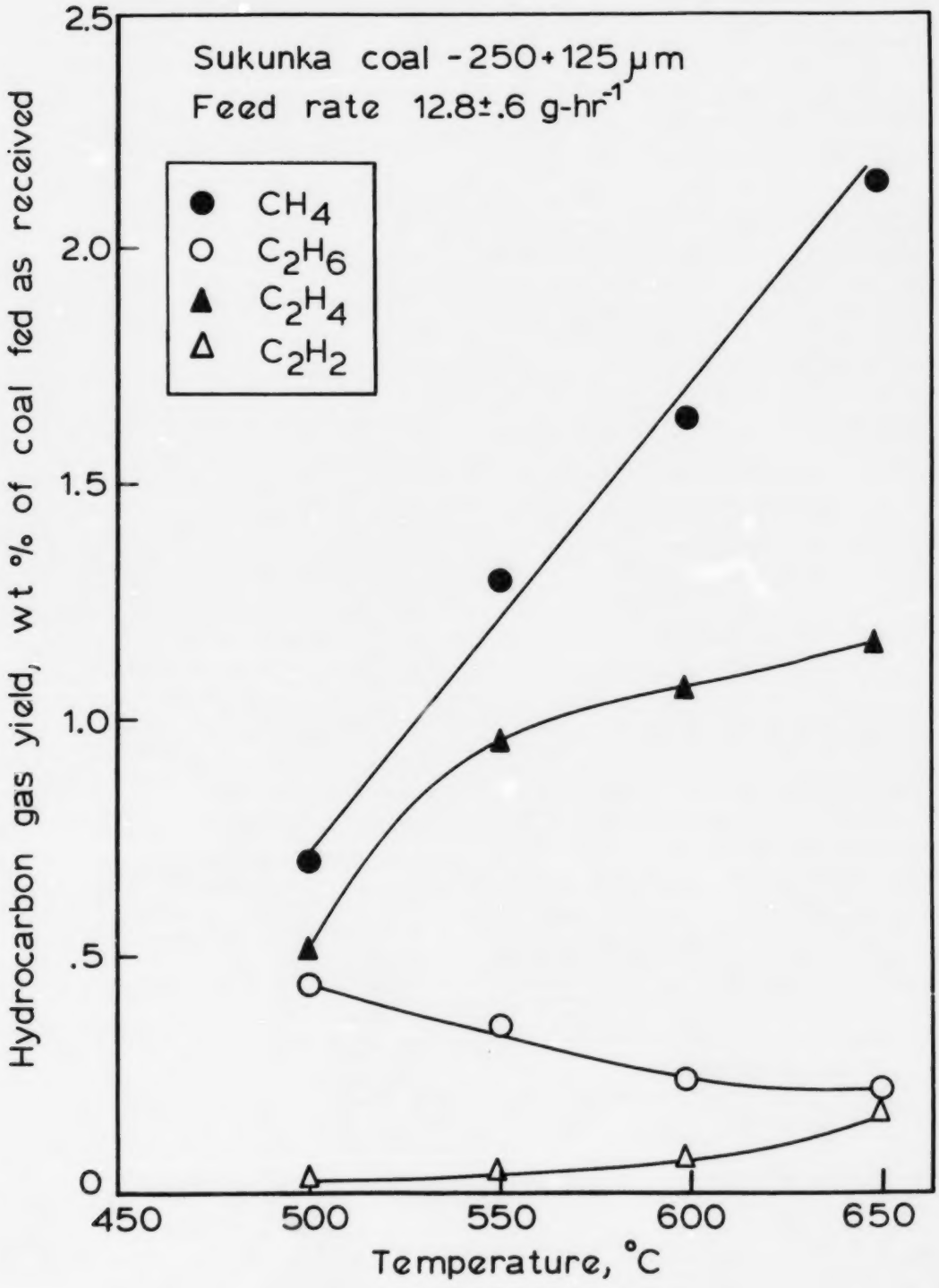


FIGURE 13

Effect of Temperature on Gas Yield

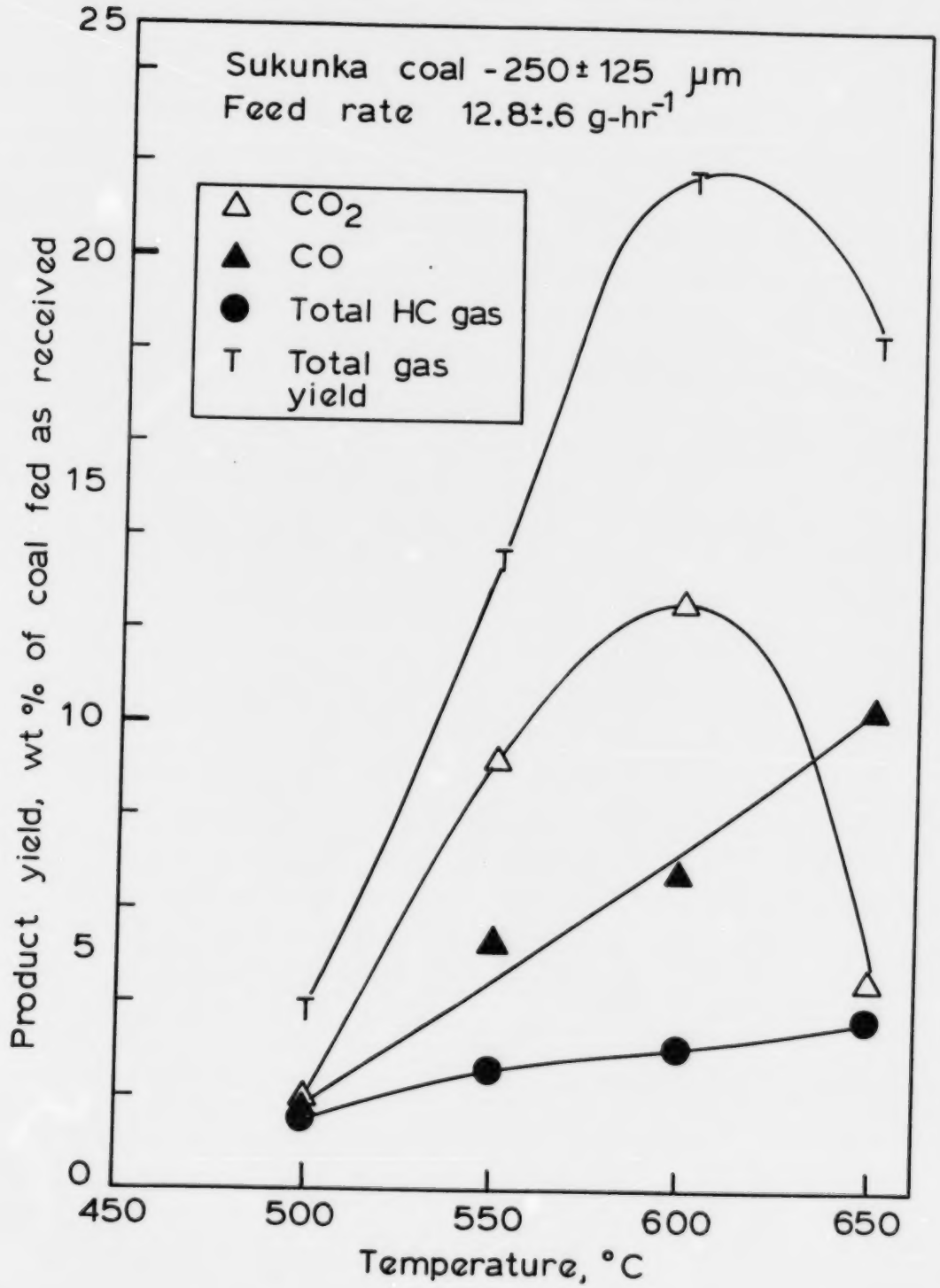


FIGURE 14

Effect of Temperature on Hydrocarbon Gas Yield

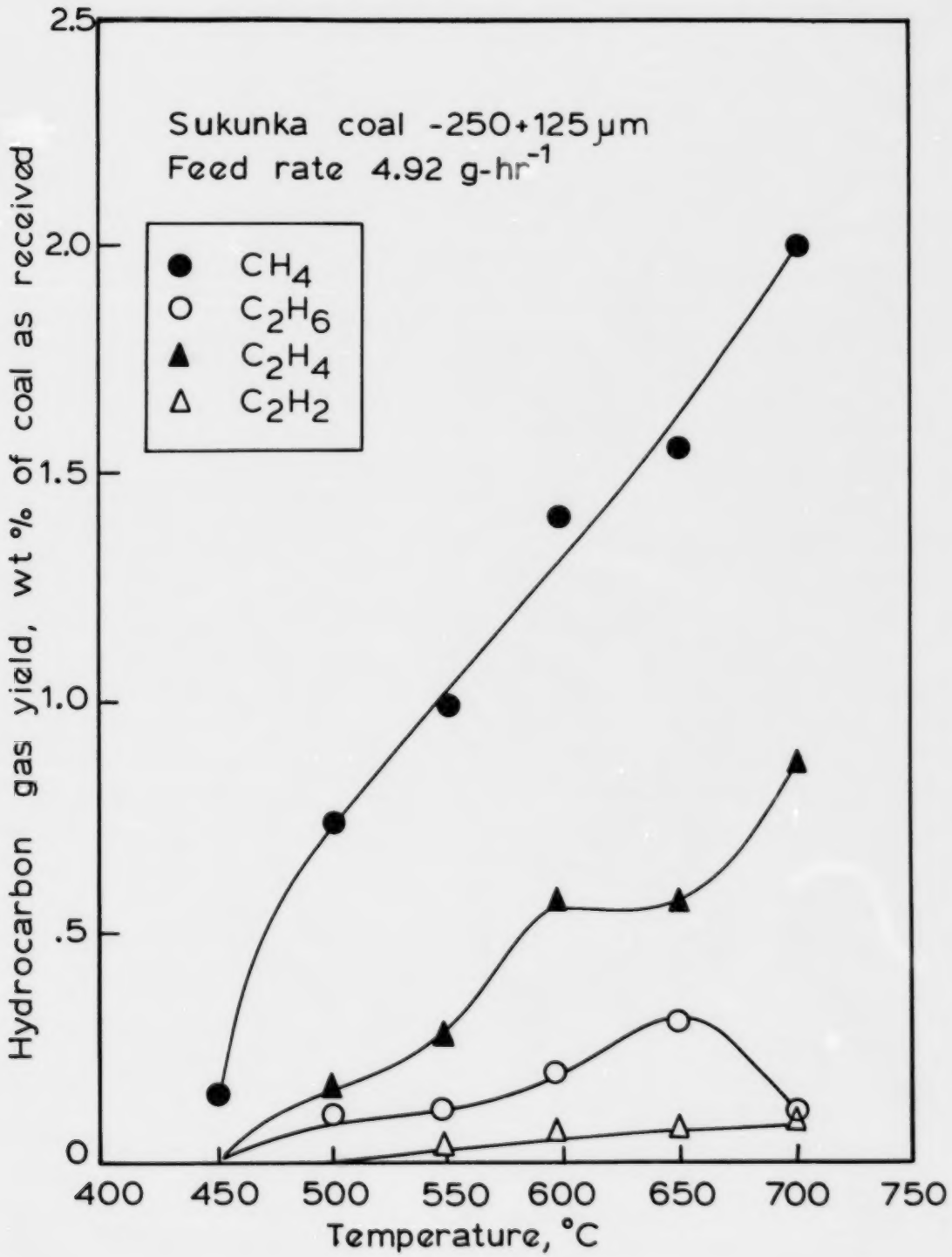
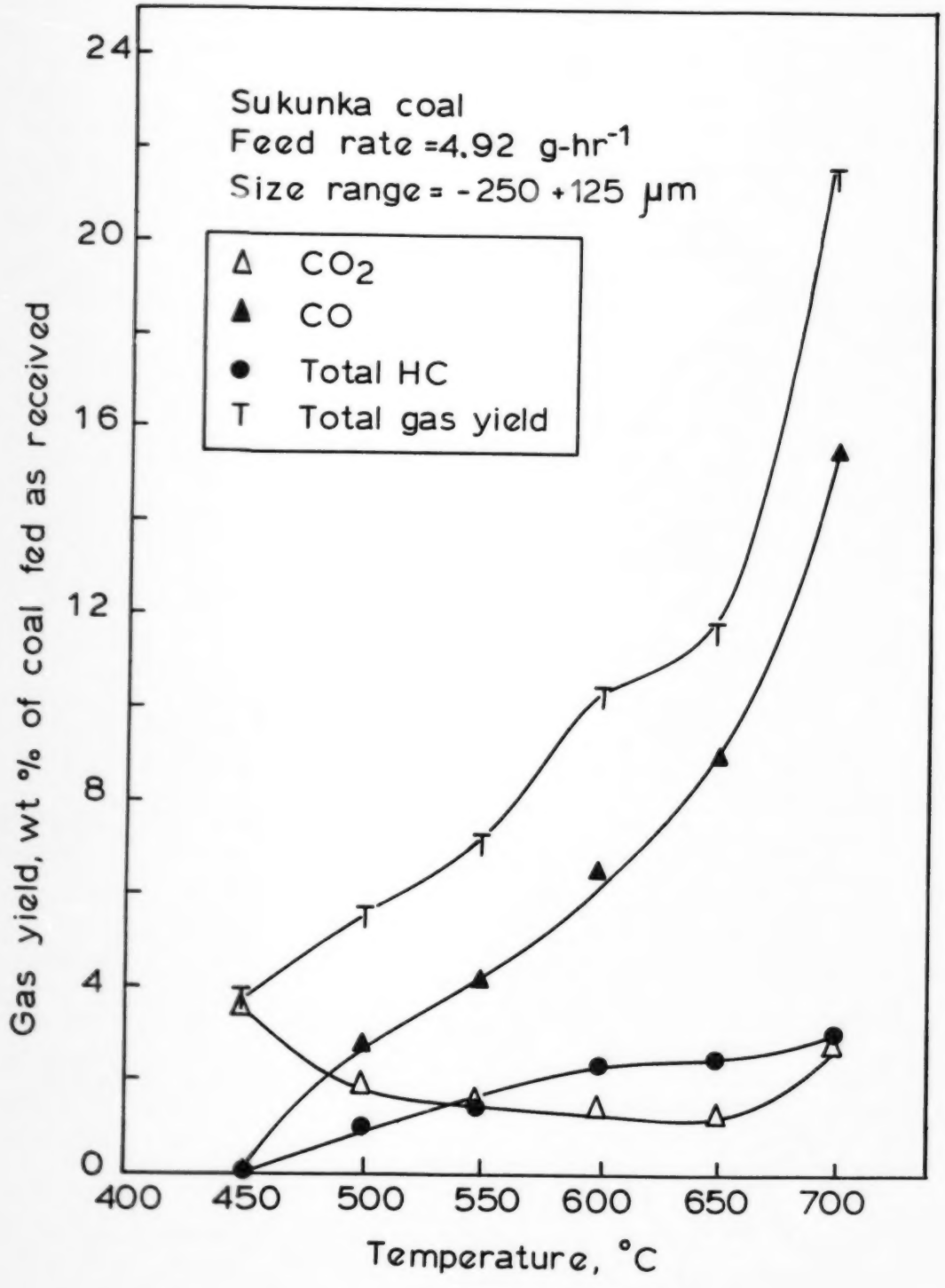


FIGURE 15

Effect of Temperature on Gas Yield



5. DEVELOPMENT OF THE SEPARATION SCHEME FOR CHARACTERIZATION OF HYDROCARBONS IN COAL TARS

Detailed knowledge of the composition of coal derived liquids is of great importance in evaluating the conversion processes, in determining upgrading process needs and for maximum benefit of end-use. Coal tar (liquids), produced by pyrolysis have remained a poorly characterized mixture of chemicals. Liquids contain a wide range of compounds with a variety of functionalities and polarities, and with a broad molecular weight distribution.

For the purpose of this project the most important type of components in the tar liquids are the hydrocarbons, which are comprised of paraffins, olefins, naphthalenes, alkyl substituted benzenes and polynuclear aromatics. In this study, it was decided to combine the advantages of "classical" methods, such as flash chromatography and spinning band distillation with advanced chromatographic methods, such as high performance liquid chromatography (HPLC) and capillary high resolution gas chromatography (HRGC).

In practice, it is unrealistic to resolve and characterize all components in the coal tar by a single step analysis without a pre-fractionation step. A pre-fractionation scheme is therefore essential in order to reduce the complexity of each analysis. The subsequent fractions are then analyzed by a combination of analytical methods, as HPLC, capillary HRGC-Mass spectrometry (MS) and other ancillary chemical spectroscopic methods.

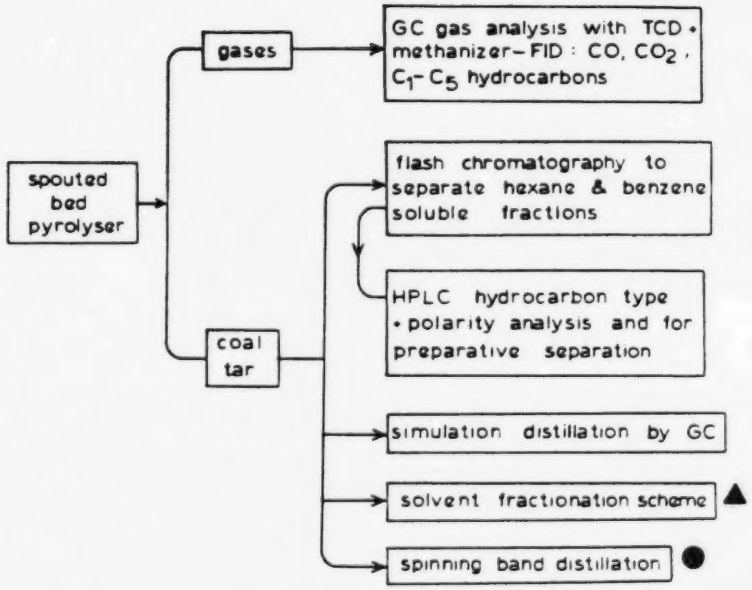
The general approach adopted for this characterization (Figures 16 and 17) involved the adoption and modification of methods appearing in the literature over the last decade. Two essential approaches were undertaken, namely:

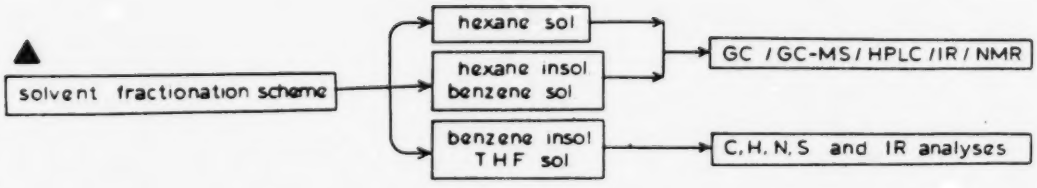
(1) Pre-fractionation scheme - to reduce the complexity of coal tar and thereby separate the tar into meaningful fractions.

(2) Detailed separation and characterization - to separate and thereby identify the individual compound present in the fractions.

FIGURE 16

FRACTIONATION-CHARACTERIZATION SCHEME FOR COAL DERIVED LIQUIDS (REVISED)


spouted bed pyrolyser
gases
GC gas analysis with TCD + methanizer-FID : CO, CO_2, C_1-C_5 hydrocarbons
coal tar
flash chromatography to separate hexane & benzene soluble fractions
HPLC hydrocarbon type + polarity analysis and for preparative separation
simulation distillation by GC
solvent fractionation scheme ▲
spinning band distillation ●


▲
solvent fractionation scheme
hexane sol
hexane insol benzene sol
benzene insol THF sol
GC / GC-MS / HPLC / IR / NMR
C, H, N, S and IR analyses

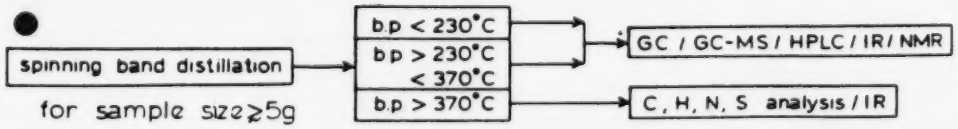
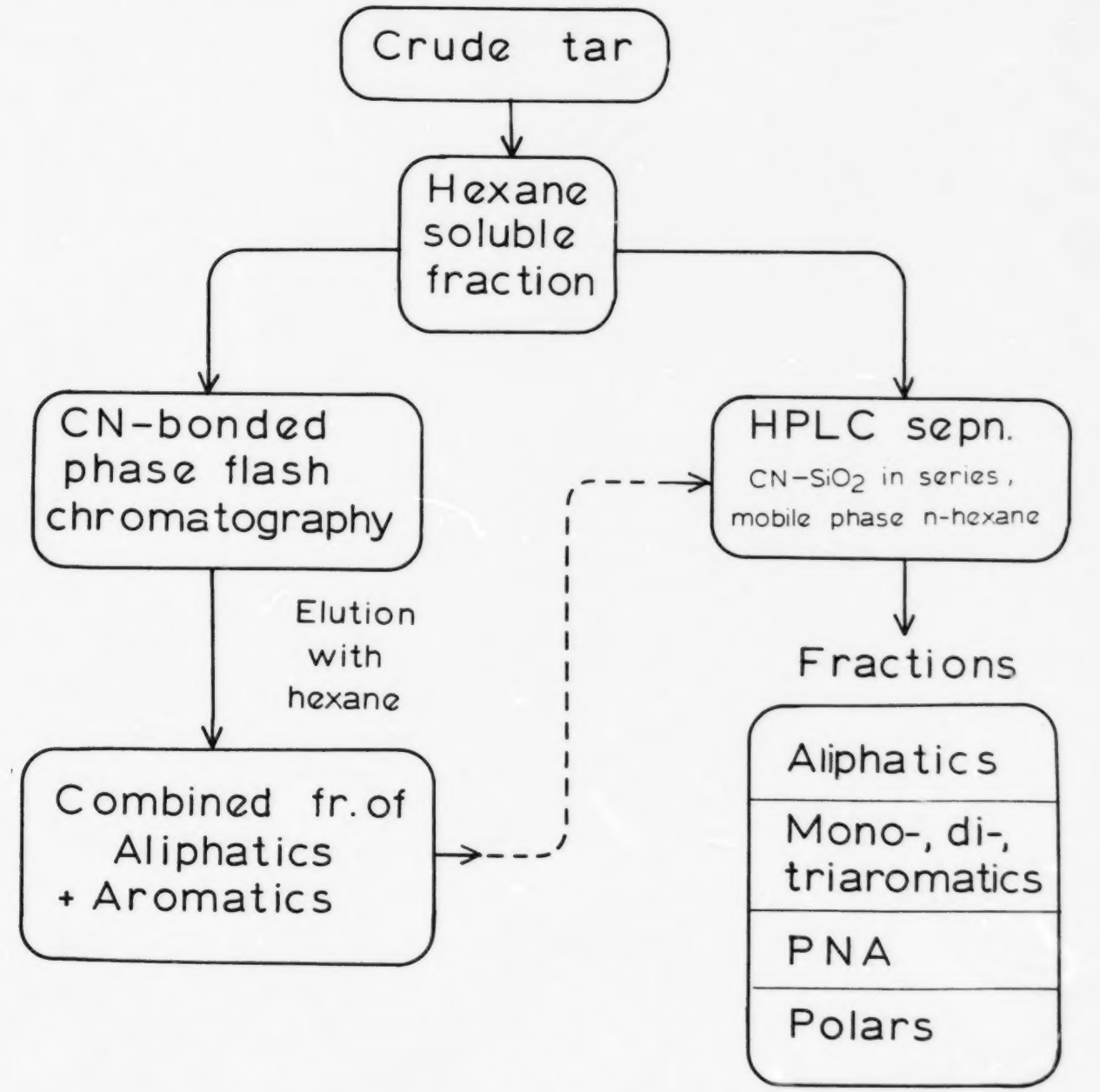


FIGURE 17

SEPARATION AND CHARACTERIZATION SCHEME OF COAL TAR



(a) Prefractionation

Two principal pre-fractionation schemes were designed and refined based on two different physico-chemical properties of coal tars. Scheme I was based on solubility classification, using a solvent sequence with increasing polarity from hexane benzene to tetrahydrofuran (Table 5). Scheme II was reliant on the volatility separation by spinning band distillation into a number of desirable cuts of different boiling ranges (Table 5) where a larger sample is available (>5g). The two pre-fractionation schemes outlined above complement each other on the basis of homologeous types and molecular weight distribution in coal tar.

(b) Hydrocarbon Group-type Analysis by Combined HPLC and Capillary HRGC

Complex hydrocarbon mixtures, such as coal tars, are best evaluated according to the amounts of hydrocarbons of each functional group-type, as saturated paraffins, unsaturated olefins, naphthalenes and aromatics. This is generally referred to as "PONA" analysis in hydrocarbon research. There are several approaches to the problem depending upon the information desired for the appropriate characterization. In this study the following two-level approach has been adopted.

Level I Analysis - a classification type analysis, comprised of the following analytical methods:

(1) HPLC method. A Varian Vista 54 Liquid Chromatograph System equipped with data station, variable wavelength UV detector and refractive index detector (RI) is used for the PONA hydrocarbon analysis of the tars. A nitrile bonded phase column (Micropak CN-10) and a silica gel column (Micropak Si-5) are used in series (Figure 18). Dry hexane was used as the mobile phase. A 6-port switching valve is used for the normal and blackflush modes during the analysis. The HPLC method could also provide mg range of relatively cleaned aliphatic hydrocarbon fractions for further analysis. A typical run takes 25-35 minutes. The difficulty

TABLE 5

Separation Scheme I - Solubility Classification

Solvent Polarity ↓ Increase	
	(1) Pentane (or Hexane) soluble
	(2) Pentane insoluble - benzene soluble
	(3) Benzene insoluble - tetrahydrofurane (THF) soluble (a)

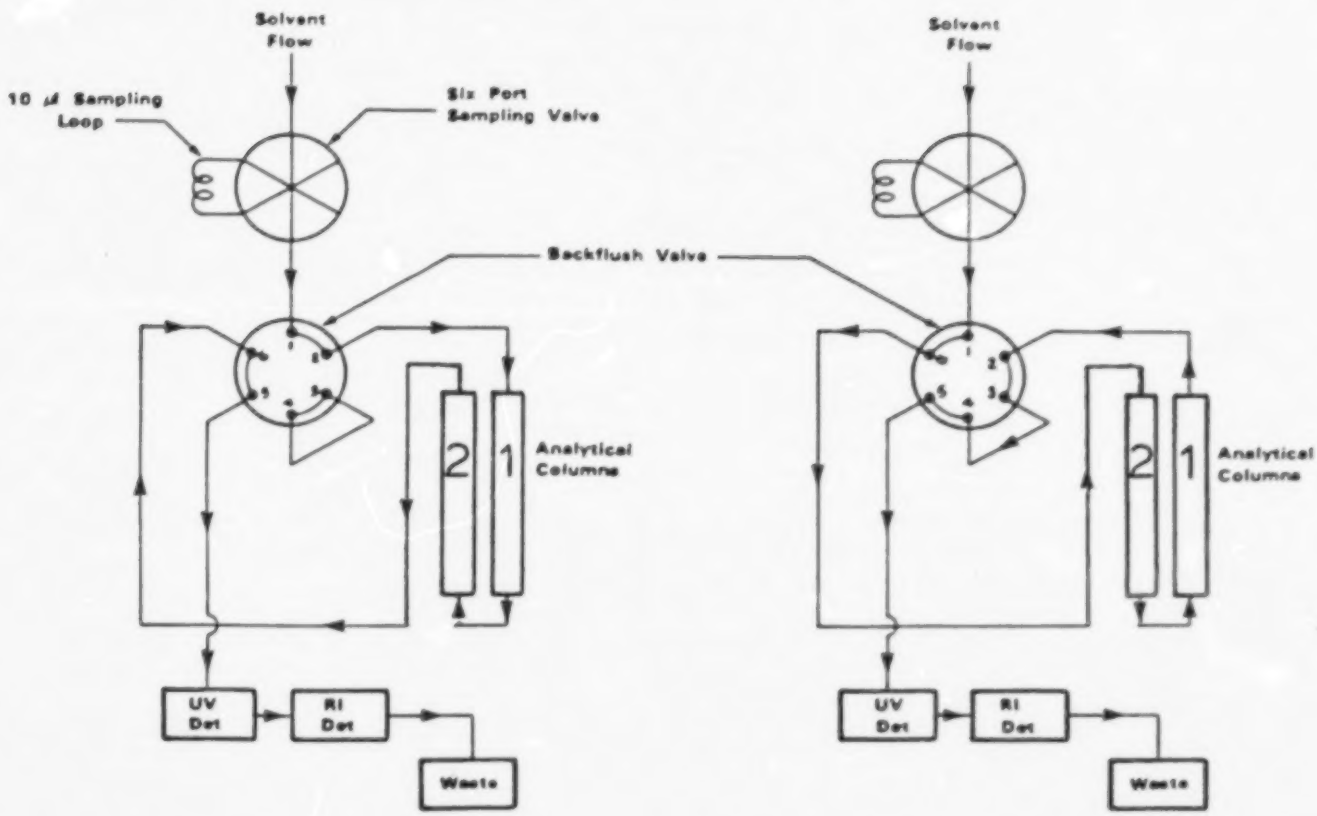
(a) It was found that coal tars generated in this study are completely solubilized in THF. For aged coal tars pyridine might be required for complete solubilization.

Separation Scheme II - Volatility Classification

Molecular Wt. and/or Polarity ↓ Increase	
	(1) boiling point (b.p.) < 230°C
	(2) b.p. between 230 - 370°C
	(3) b.p. between 370 - 540°C
	(4) b.p. > 540°C

FIGURE 18

DUAL COLUMN HPLC TECHNIQUE



Column 1 : Micro-Pak CN / 4mmx30cm
Column 2 : Micro-Pak Si / 4mmx30cm

here is the determination of adequate response factors.

(2) Simulation distillation (SIMDIS) by packed column GC. The boiling range of a potential hydrocarbon fuel liquid is one of its chief specifications, partly because distillation is one of the principal processes to separate one product from the other. Conventional distillation procedures are lengthy and besides requires a larger sample. Currently, the ASTM D2887 is under revision. Simulated distillation has gained widespread acceptance by the hydrocarbon processing industries, and application of this technique to coal derived hydrocarbon liquids is feasible.

Level II Analysis - a detailed analysis on the separated or fractionated fractions. A Hewlett Packard high resolution capillary GC-MS system (Model 5985B) was used for detailed compositional study. A selective mass ion scanning method was used to refine and mapping the low molecular weight aromatic hydrocarbons, ranging from alkyl substituted benzenes to alkyl substituted naphthalenes.

6. COMPARISON OF THE HEXANE SOLUBLE FRACTIONS (OILS) FROM THE MINIATURE AND AND BENCH SCALE PYROLYZERS

Figures 16 and 17 outline the method for detailed characterization of the hexane soluble fractions.

The Dual column HPLC method (Figure 18) was used in the following study. Aliphatic hydrocarbon paraffins and olefins pass through the moderately polar CN column unresolved but are separated on the polar Si column where the paraffins elute first followed by the olefins. Aromatics are retained longer on the CN and Si columns, and elute next. After elution of the aromatic hydrocarbons, the backflush valve is actuated and the polar components elute from the CN column as a single peak.

Coal tar liquids generated from a bench scale 2kg/h spouted-bed pyrolyzer were kindly provided by A. Jarallah; some preliminary result on the characterization of hexane soluble fractions are illustrated as follows:

Origins of coal: Sukunka Bituminous coal

Coal Tar Sample (Run #)	Pyrolysis Temperature °C
59	540°C
64	560
67	580
61	640

(a) Procedure

(1) The tar liquid sample ~ 200 mg was fractionated by using a 3 ml CN extraction column (Baker) using 2 x 2 ml dry hexane. The first 2 ml hexane elute was clear and the second 2 ml hexane elute exhibited a pale green fluorescence.

(2) 10 µl of the first 2 ml hexane elute was used in the dual column HPLC separation under the following instrumentation conditions.

Temperature = 30°C mobile phase = hexane

Flow rate = 1.5 ml/min pressure = 94-98 atmospheres

UV detector λ = 235 mm RI detector = energy level 0.5

Backflush time set at 12 to 15 min.

Overall chromatographic time = 24 to 36 minutes

HPLC fraction collection time

aliphatic HC = 4.7 - 5.2 min.

aromatic HC = 5.2 - 9 min.

polynuclear aromatic HC = 9 - 12 min.

polar component ~ 23 min.

Detector output is shown as Figure 18 for Run 64.

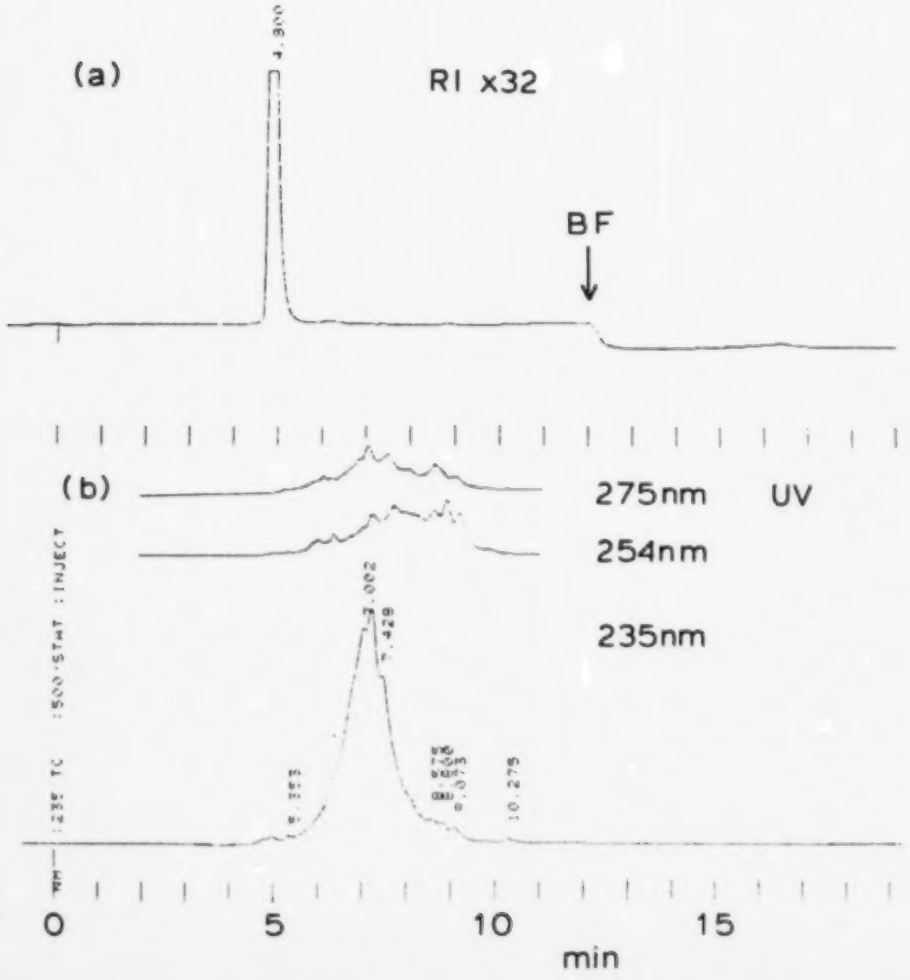
(3) The aliphatic hydrocarbon fraction was routinely analyzed on the capillary HRGC on a wide-bore fused silica capillary SE-30 column (15 meters). Instrumentation conditions were set as follows:

Initial 40°C (6 min)-5°C/min to 100°C(2 min)-10°C/min to 180°C(5 min)

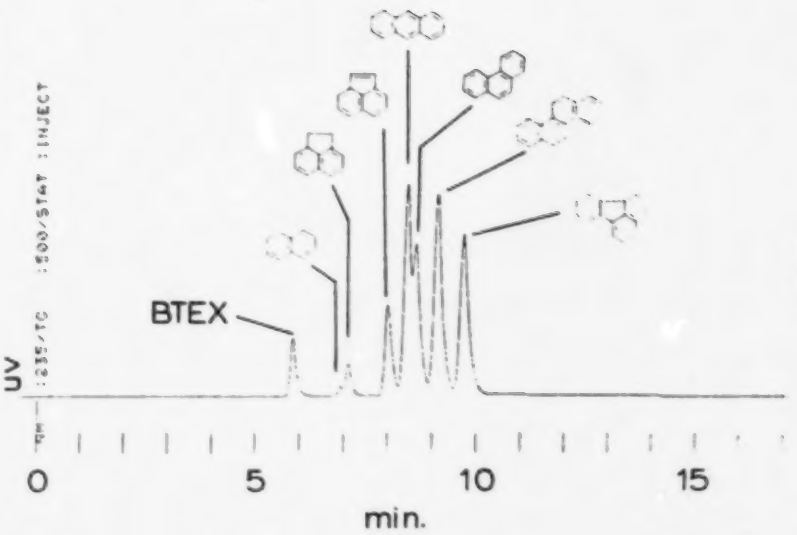
(4) Detailed assignments were done by HRGC-MS: a wide-bore fused silica

FIGURE 19

HPLC OF COMBINED ALIPHATIC AND AROMATIC FRACTION SEPARATED BY CN BONDED PHASE FLASH CHROMATOGRAPHY



(c)



(BTEX = ⬡ + ⬡ + ⬡ + ⬡)

(a) Refractive index (RI) output for the aliphatic sub-fraction. BF= backflush at 12 minutes.
(b) UV output of the aromatic sub-fraction at different wavelength (λ) 235 μm shown to provide the best sensivity for the alkylbenzenes and alkylnaphthalenes.
(c) Model compound study to illustrate the HPLC assignments.

capillary DV-5 column (25 meters) was used throughout all HRGC-MS works. Instrumentation conditions were set as follows:

HRGC: $60^{o}C$(1 min)-$5^{o}C$/min to $90^{o}C$-$2^{o}C$/min to $180^{o}C$

MS: at electron impact mode (70 eV); mass range 38-490 amu/0.6 sec.

(b) Results and Discussion

The high resolution GC chromatograms (Figure 20) for the separated hexane soluble aliphatic hydrocarbon fraction from the HPLC separation of the CN-flash chromatographic hexane eluted fraction #1 show the samples to have similar GC chromatographic peak structure. This result suggests that the aliphatic hydrocarbon oils produced from the same coal under different pyrolytic temperature retain essentially the same oil composition, although the oil yield derived from the solvent fractionation might vary with the pyrolytic temperature (Table 2). The detailed assignments of the HRGC-MS output (Figure 21) are collected in Table 6 for the aliphatic oil fraction produced from Jarallah's pyrolysis run #64 (cf $560^{o}C$).

As expected from the designed separation scheme the alkanes (i.e. paraffins) dominate this particular aliphatic hydrocarbon oil fraction. Only one major type of alkanes were identified, the iso-alkanes, which in turn is dominated by C_{10} subsequent by C_9, C_{12} and C_{13}. From the FID output of HRGC and the total ion current output of HRGC-MS the average molecular weight of this aliphatic hydrocarbon oil is estimated to be around 152.

Unfortunately, all the light hydrocarbons were not found in this oil fraction provided by Jarallah, as a consequence of the sample handling.

Due to the improved technique in trapping the coal tar gas and vapor in the present miniature scale work, a high recovery of more volatile components associated with the tar can be achieved. The hexane soluble fraction of the tar obtained from the pyrolysis of Sukunka coal at $500^{o}C$ (Run #8) was flash chromatographed on the CN-bonded phase extraction column. The hexane eluate was used

FIGURE 20

HRGC Chromatograms of Some Aliphatic Sub-fractions from Larger Unit

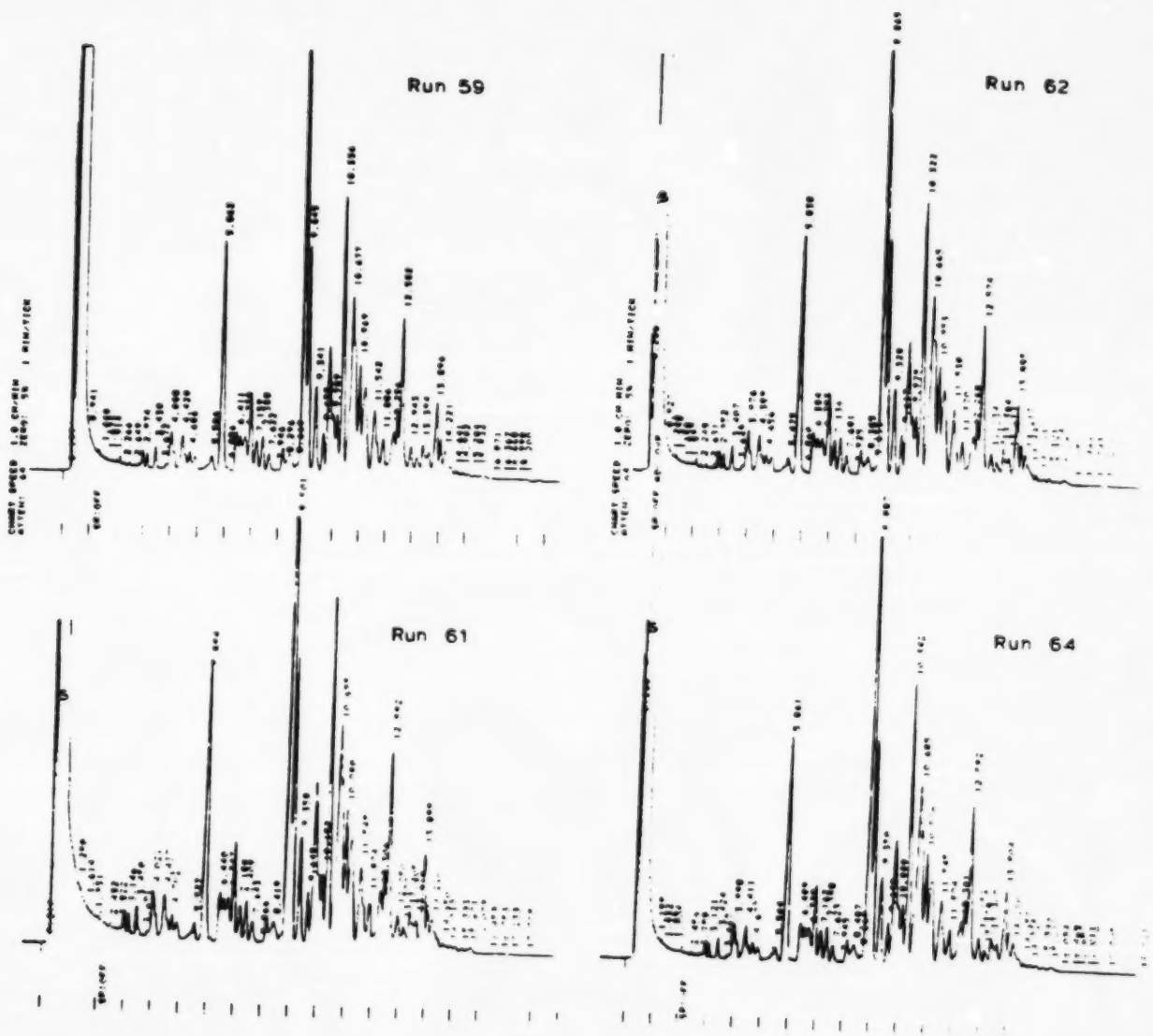
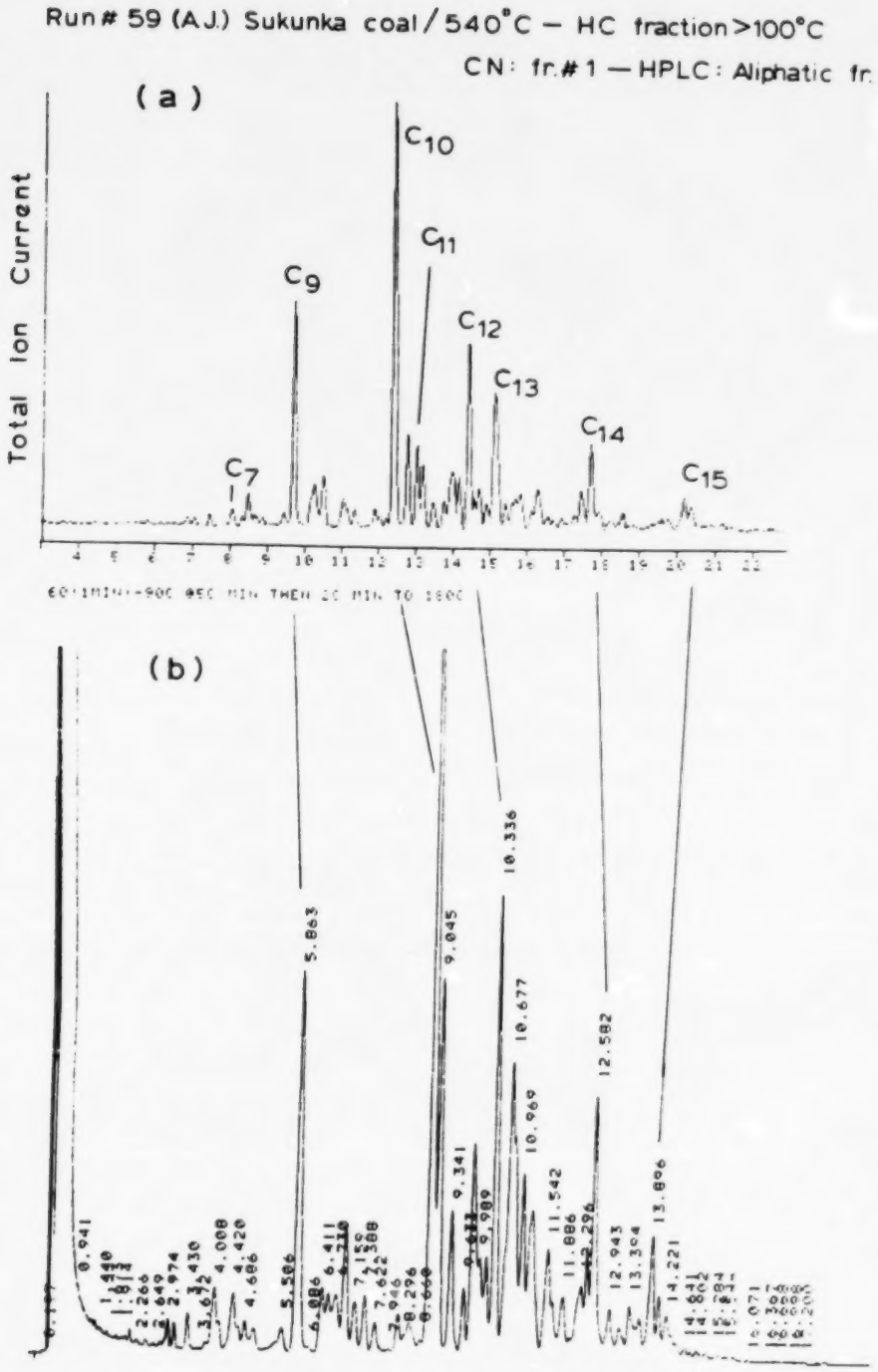


FIGURE 21



Chromatrograms of isolated aliphatic hydrocarbon fraction

(a) Total ion current output from HP HRGC-MS

(b) FID output from Varian capillary HRGC

TABLE 6

Tentative assignment of aliphatic hydrocarbon fraction from the pyrolysis of Sukunka coal on bench scale unit

Retention time, min	Assignment (b)
2.649	N.I.
2.974	N.I.
3.430	2-methyloctane
4.008	2,4-dimethylpentane
4.111	4-methylhexene
4.420	2,3-dimethylcyclobutanone
5.506	4-methyl-1-pentene-3-one
5.863	2,5-dimethylheptane + 2,2,5-trimethylhexane
6.411	3-methyloctane + 2,2,3-trimethylhexane
6.556	2,2,3,4-trimethylpentane + 3-ethyl-2,2-dimethylpentane
6.730	N.I.
6.941	2,5-dimethylheptane
7.159	5-ethyl-2-methylheptane + 3-methylnonane
7.388	N.I.
7.622	2,2,5,5-tetramethyl-3-hexene
7.946	N.I.
8.149	N.I.
8.296	N.I.
8.396	N.I.
8.883	2,2,4-trimethylheptane + 2,6-dimethyloctane
9.045	2,2,6-trimethyloctane
9.341	6-ethyl-2-methyloctane + undecane
9.633	2,3,7-trimethyloctane
9.829	5,6-dimethyldecane
9.989	2-methylundecane + 3,7-dimethylnonane
10.140	3,4-dimethyldecane
10.336	U.I. (parent peak M^+=155 probably a N-containing species
10.667(left shoulder)	2,2,3-trimethylnonane + branched $C_{12}H_{26}$ and/or $C_{13}H_{28}$
10.667	2,3-dimethylundecane
10.969	N.I.
11.178	branched $C_{12}H_{26}$ and/or $C_{13}H_{28}$
11.542,11.645	branched $C_{13}H_{28}$

TABLE 6
(cont'd)

Retention time, min	Assignment (b)
11.886	2,3,4-trimethyldecane + 3,3-dimethylundecane
12.055	N.I.
12.296,12.426,12.582	branched $C_{14}H_{30}$
12.943,13.165	N.I.
13.896	2,6,11-trimethyldodecane
14.048,14.221	branched $C_{16}H_{34}$

(a) Containing mostly aliphatic saturated hydrocarbons (i.e. alkanes) from approximately C_7 to C_{16}
(b) Tentative assignment, subjected to future refinement; U.I. = unidentified

without further preparative separation by HPLC method. It is therefore expected that light hydrocarbons (aliphatic C_8 and below plus simple substituted benzenes) together with aliphatic C_{20} or higher and di-aromatics are within the investigation range.

Total ion current output (Figure 22) in conjunction with the selective mass ion scanning (Figure 23) positively identified the presence of benzene, toluene, ethylbenzene, 1,2- and 1,4-dimethylbenzene, six C_3-benzenes, eleven C_4-benzenes, 1H-indene,naphthalene, three methylnaphthalenes, several C_3 and C_4-naphthalenes and aliphatic C_9 to C_{30}. It was interesting to note that aliphatic hydrocarbons are present to a lesser extent than are the aromatic counterparts. The aliphatic hydrocarbons C_9-C_{15} were found as indicated by the dotted envelope line in Figure 22, which appears to have similar distribution as in Figure 20a. A significant portion of C_{28} and C_{30} were identified, which might be of importance as biological markers or chemical fossils in this particular coal.

FIGURE 22

Total ion current output of hexane eluted CN bonded phase flash chromatographic fraction of coal tar from Sukunka coal (Run # 8 at 500°C)

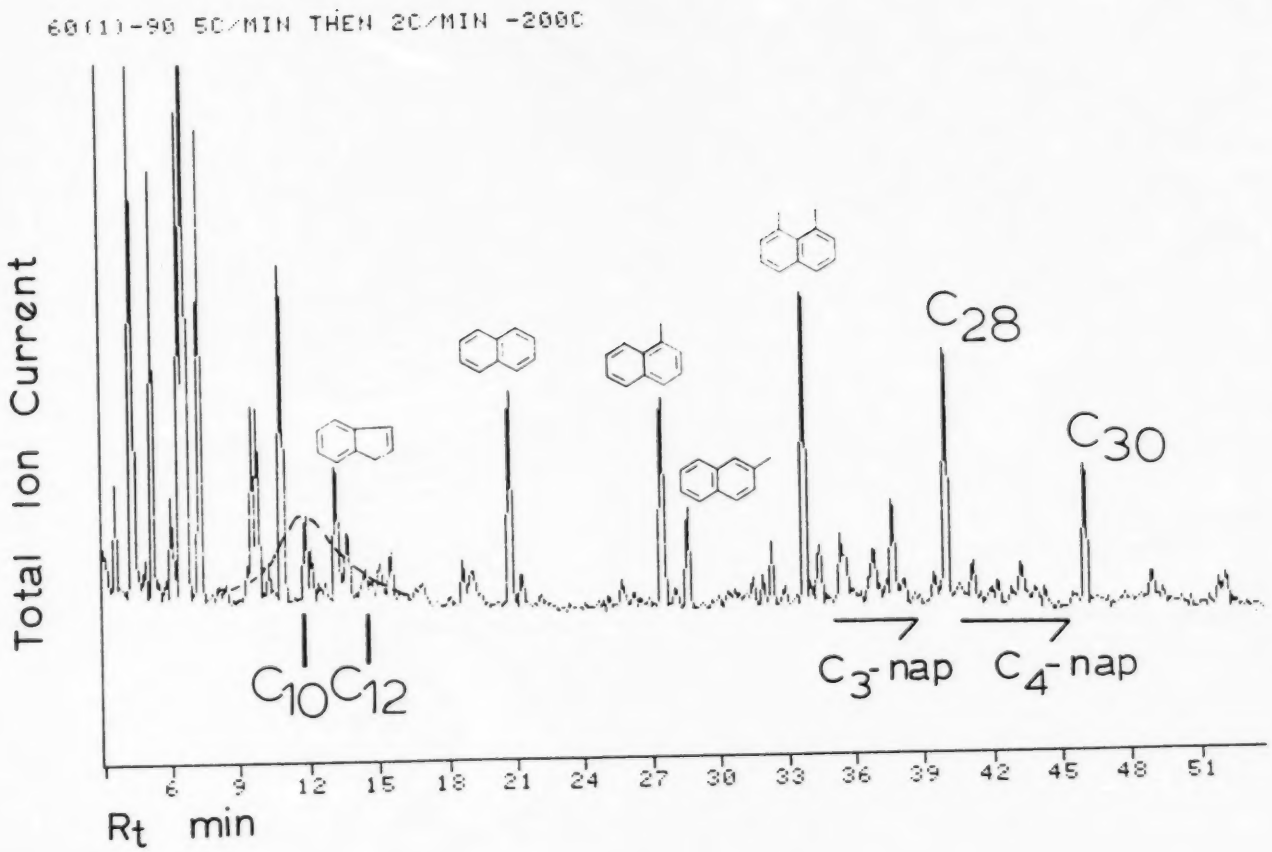
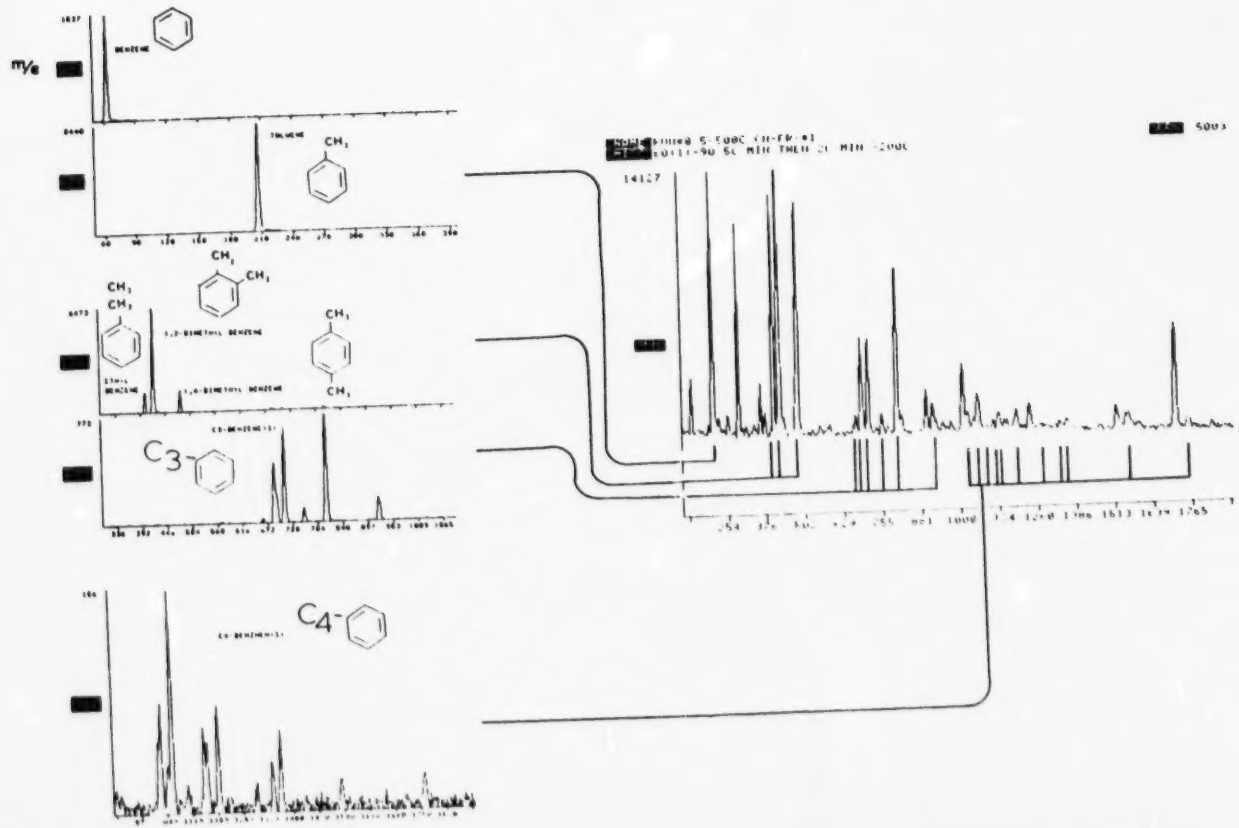


FIGURE 23

Selective Mass Ion Scanning

Total Ion Current Output



7. CONCLUSIONS AND FUTURE WORK

1. The major emphasis in the first twelve months was to devise an operable pyrolysis system and analytical framework for the detailed study of the products. A miniature spouted bed pyrolysis reactor was developed and tested. The benefits of operating with a spouted bed were demonstrated by the trouble-free operation experienced for the highly-caking Sukunka coal.

2. A cryogenic and solvent trapping unit permitted essentially total recovery of light hydrocarbons generated from pyrolysis runs. Permanent gases were analyzed by G.C.

3. A logical separation and characterization scheme for the hydrocarbon fraction was developed, modified and tested based on the classical classification concept of coal liquid products (solvent fractionation and distillation) and on modern analytical instrumentation (flash chromatography, HPLC, HRGC, HRGC-MS).

4. Alkanes (C_9 - C_{30}), C_1 - C_4 - alkylbenzenes and C_1 - C_4 - alkylnaphthalenes were positively identified in coal tars derived from pyrolysis of Sukunka coal. The alkane sub-fraction (C_9 to ~C_{16}) was found reasonably identical in terms of composition present all Sukunka coal tars generated in the miniature and in a bench scale unit, and at a range of temperature and particle size.

5. Analysis of these Sukunka tars are as yet incomplete. Polynuclear aromatics and polar compounds are yet to be determined. Facilities for simulated distillation, and spinning band distillation are set up, but no liquids have yet been tested.

6. The proposed work statement for 1983-84 is given in Appendix B, the major thrust of which is to complete item 5 above, and extend the work to a series of other coals.

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6. A.M. Al-Jarallah, "Pyrolysis of Some Western Canadian Coals in a Spouted Bed Reactor", Ph.D. Thesis, April, 1983, The University of British Columbia, Canada.

7. Z. J. Stompel, K.D. Bartle and B. Frere, "Structural Analysis of Tars from Fluidized Bed Pyrolysis of Coals", Fuel, 61, 817 (1982).

8. J.B. Howard, "Fundamentals of Coal Pyrolysis and Hydropyrolysis" in Chemistry of Coal Utilization , Second Supplementary Volume, ed. by M.A. Elliott, John Wiley & Son Inc., 1981, pages 665-784.

APPENDIX A

Personnel

For the period of 1982-83 the project was manned by the Principal Investigator and Dr. K.C. Teo (Senior Research Scientist). In late August, Miss Diane J. Jung was hired as the Junior Chemist to assist the established routine analysis, starting 6 September.

Paper and Conference

K.C. Teo presented a paper entitled "Characterization of Coal Liquids by a Combination of HPLC and GC-MS methods" at the 66th Chemical Conference at Calgary (June 8, 1983). This paper will be finalized and submitted for publication in an international journal in the near future.

TABLE: Project Budget and Committed Expenditure 1982-83 (16 Aug.,1982-31 Mar.,1983)

Item	Committed Expenditure*	Contract Budget
1. Labour		
a) Research Associate (Dr. K.C. Teo)	23,417	23,090
b) Fringe Benefits	1,488	est. 1,193.25
Sub total	24,905	24,283.25
2. Equipment		
a) Varian High Resolution GC	33,808	
b) Perkin-Elmer Spinning Band Still	6,055	
c) Biichi Rotavapor	2,497	
d) Pyrolysis Unit	5,500	
	47,860	50,700
3. Supplies	14,706	5,900
4. Subcontracts	2,908	570
5. Travel and Living	1,167	750
6. Overheads	4,832	9,302.54
Total	96,378	92,380.98

* Exact figures have been billed by the U.B.C. Finance Department.

APPENDIX B

Proposed Major Tasks of Characterization of Liquids Fuels from Spouted Bed Pyrolysis of Canadian Coals

1983-1984
DSS File 20SU 23440-2-9093

Objectives

1. The simplicity of operating the miniature spouted-bed reactor for pyrolysis run of Canadian coals would be of great advantage in the screening of suitable Canadian coals for maximizing tar yields. For the period of 1983-84 a series of pyrolysis runs will be attempted to demonstrate feasibility for a wider range of coals in terms of
   a) coal rank (lignite, subbituminous and bituminous)
   b) caking and non-caking coals
   c) geological area of origin and
   d) oxygen and sulfur contents
2. Work will be continued on the characterization of coal products, with primary emphasis on coal liquids produced in this study. Analyses on the quality of coal liquids will be continued and developed in the current direction using state-of-the-art in modern analytical instrumentation. The three different forms of products, namely gas, liquid (tar) and solid (char) are to be characterized by different analytical techniques outlined and summarised below:
   a) Gaseous product: usually contains the entrainment gas N_2 (major component) with H_2, CO, CO_2 and light hydrocarbons from C_1 to C_5/C_6. The existing Varian High Resolution Gas Chromatograph unit which currently operates on a dual-column switching valve technique and/or selective column method can extend the gas analysis up to C_5/C_6 and possibly some lower aromatic hydrocarbons.

2. b) Coal tar: detailed characterization will be centered on hydrocarbons based on the current refined separation and hydrocarbon type analysis. Emphasis will be on the integration of bonded phase flash chromatography, high performance liquid chromatography (HPLC) and gas chromatography-mass spectrometry (GC-MS) for detailed identification. Simulated distillation by GC will be included along with the characterization of the hydrocarbon fractions. Work will be continued for methodological development for quantitation of different hydrocarbon classes present in tars. In other words, research into feasible calibration methods to quantify

(i) Aliphatic hydrocarbon (C_7-C_{18} or higher)

(ii) Alkylbenzenes

(iii) Alkylnaphthalenes

(iv) Polynuclear aromatics

c) Char: proximate analysis will be conducted in house by thermal gravimetric analysis (TGA) and ultimated analysis to be contracted out to a local commercial analytical service. Samples will be sent to CANMET for further petrographic characterization.

Major Tasks
(N.B. Detailed analysis will be included with each task)

Task 1 Pyrolysis of Forestburg and Fording coals and detailed characterization of hydrocarbon fractions plus simulation distillation data of these fractions.

1 September-31 October

Task 2 Pyrolysis of Onakawana lignite. This will be the first test of a lignite using spouted bed pyrolyzer. This will require some exploration on the establishment of pyrolysis temperatures and attention on the characterization of oxygenated hydrocarbons, such as alcohols and ketones. 1 November-31 December

Task 3 Pyrolysis of Devco and Minto coals. This will provide key source of information regarding the feasibility of using spouted bed reactor for the high

sulfur Eastern coals. Some attention will be paid to the characterization of organo-sulfur compounds present in tar. 2 January-29 February

Task 4 Assemble data and write up report. 1-31 March

CHARACTERIZATION OF LIQUID FUELS FROM SPOUTED BED PYROLYSIS OF CANADIAN COALS

PROJECT SCHEDULE 1983-84 (REVISED SEPT. 1983)